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BROMINE ADDITION COMPOUNDS OF DIMETHYLANILINE.[1]

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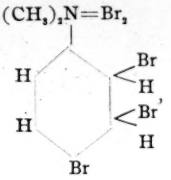
The work described in this paper was begun in January, 1904, and had made much progress before the summer of that year, when we received a paper by K. Fries[2] on the action of bromine on salts of dimethylaniline. At first sight it seemed as if we should be obliged to give up our work to avoid intruding on the field reserved by him, but a more careful comparison of his products with ours showed that they belonged to different series of compounds, for, whereas his substances were perbromides, in which bromine was united to bromine, in ours the bromine was united either to the benzene ring or directly to the nitrogen. We have, therefore, continued our work, but when, in the course of it, we have encountered per-

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by Latham Clarke.

[2] Ber. d. chem. Ges., **37**, 2338 (1904).

bromides, we have dropped the study of them as soon as we had ascertained that they belonged in the field reserved by Dr. Fries.

Nomenclature.—Bromine enters into the molecules of the substances described in this paper in four different ways; it is necessary, therefore, to contrive names to distinguish them, and any such nomenclature must be founded on the usual distinction of brom compounds for those formed by substitution and bromides for those formed by addition. The addition compounds, in which the bromine is attached to the ring, we propose to call benzbromides; those where it is attached to the nitrogen, amine dibromides (or hydrobromides); those where it is attached to bromine, perbromides, as at present. The use of these names is illustrated in that of the following compound,



benzdibromide of dimethylbromphenylamine dibromide—a clumsy name, but one which expresses the constitution as simply as possible.

The perbromides of dimethylaniline, prepared by Fries, are:

$C_6H_4BrN(CH_3)_2HBr_2$,
$C_6H_4BrN(CH_3)_2HBr_4$,
$(C_6H_3Br_2N(CH_3)_2HBr_2)_2Br$,
and $C_6H_3Br_2N(CH_3)_2HBr_3$.

These were prepared by adding bromine to the hydrobromide, or to the free dimethylaniline dissolved in glacial acetic acid. Our compounds were made by adding bromine to dimethylaniline diluted with chloroform; in this way we obtained the addition of 2, 4 or 6 atoms of bromine and, as there is so little difference in the two methods of preparation, it is necessary

first to show that our products belong to a different series from those of Fries.

The structure of our addition compound containing 2 atoms of bromine, which melts at 82°,[1] was determined by the following experiments: By the action of potassic hydrate it is converted into parabromdimethylaniline, melting at 55°, which shows that it is an addition-, not a substitution-product; with ethyl bromide it combines, forming a compound

$$Br_2C_6H_5N(CH_3)_2C_2H_5Br,$$

therefore none of the bromine is attached to the nitrogen atom, but the 2 atoms of bromine must be attached to the benzene ring and the substance is the benzdibromide of dimethylaniline, $Br_2C_6H_5N(CH_3)_2$. This inference is confirmed by the facts, that it dissolves in dilute acids, gives no reaction with potassic iodide and is turned reddish-brown by quinone. We have shown, by experiments soon to be published, that such color reactions with quinone usually indicate a free amine. Further, as parabromdimethylaniline was formed from our dibromide, the 2 atoms of bromine are probably attached to the 3.4 atoms of carbon, although the 1.4 position is not disproved.

Our substance containing 4 atoms of bromine could be made by the action of more bromine on the preceding compound. Under these conditions Fries' perbromide,

$$C_6H_4BrN(CH_3)_2HBr_2,$$

might be formed and our product certainly resembles it in many properties; we will, therefore, first consider whether the two substances are identical. The difference between the melting-points is not great, the perbromide melting at 70°–75°, our compound at 65°–70°; this is not sufficient to establish a difference between unstable bodies like these, which decompose partially during recrystallization and completely on melting. Differences were also observed in color and crystalline form, but they cannot be considered decisive. It is necessary, therefore, to resort to differences in behavior to settle this point and,

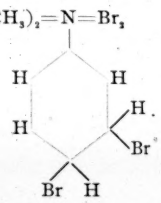
[1] The melting-points of all these addition compounds are approximate.

fortunately, the action of our compound with more bromine gives us the desired proof that the two bodies are not the same. Under these conditions it takes up 2 more atoms of bromine, giving a very unstable product with 6 atoms, which loses hydrobromic acid with great ease, dropping to a comparatively stable compound with 5 atoms of bromine. This substance is very close in composition to Fries' perbromide,

$$C_6H_3Br_2N(CH_3)_2HBr_3,$$

but is proved to be different from it by its behavior with sodic acetate in acetic acid, for, whereas the perbromide gives tribrommonomethylaniline, $C_6H_2Br_3NHCH_3$, melting at 37°, hydrobromide, melting at 202°, our substance gives liquid dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2$, hydrobromide, melting at 110°. That they are not identical is also shown by the melting-points, the perbromide melting at 102°, our body at 78°, whereas 5° is the largest inaccuracy in melting-points observed by us as due to the accidental differences in purification or taking of the melting-point frequent with such unstable compounds. As, then, our compound containing 5 atoms of bromine is not identical with that of Fries, our compound with 4 atoms of bromine must also be different from his, since his Br_5 compound is the only one that could be formed from his Br_4 compound. Further, our substance with 4 atoms of bromine cannot be any other perbromide, as it contains only 2 atoms of bromine which act on potassic iodide and the only perbromide of this composition, which could contain that number, is the one described by Fries. The bromine in this compound, then, cannot be attached to bromine, but must be either on the benzene ring or on the nitrogen. Two of the atoms are undoubtedly attached to the benzene ring, as this substance is made from the benzdibromide, which has that structure. The other 2 atoms of bromine cannot be attached to the benzene ring, as they are removed by treatment with potassic iodide (potassic bromide being formed and iodine set free) and bromine on the ring, as in the benzdibromide, does not act on potassic iodide. It follows, therefore, that they must be attached to the nitrogen atom and this conclusion is confirmed

by the fact that the compound crystallizes unaltered from ethyl bromide and gives no salt with hydrobromic acid, showing that the nitrogen atom is fully occupied. The substance must be, then, the benz-3,4-dibromide of dimethylphenylamine dibromide,



This constitution is in harmony with the other observed properties of the compound. Quinone gives no color with it. Acetone removes bromine, converting it, apparently, into the benzdibromide of dimethylaniline. Sodic thiosulphate and potassic iodide form parabromdimethylaniline. Sodic hydrate converts it into dibrom dimethylaniline; at first sight the neat formation of a dibrom compound from a substance containing bromine in the side chain might seem strange, but Fries has observed a similar phenomenon with his perbromides, and Chattaway's results[1] would show that all halogen substitutions in the ring of aromatic amines are preceded by substitution in the amino group. Alcohol gives the hydrobromide of dibromdimethylaniline by a similar reaction, followed by addition of hydrobromic acid to the dibromdimethylaniline. When it is allowed to stand in the cold, especially if moistened with chloroform, it is frequently converted, with evolution of hydrobromic acid, into a red substance, which contains 1 atom of bromine capable of replacing iodine in potassic iodide and, from its other properties, is evidently one of Fries' perbromides. Its composition is very near his

$$[C_6H_3Br_2N(CH_3)_2HBr]_2Br,$$

but it is, apparently, a different compound, as it melts at 105° instead of 135°. The way in which such a product could be formed will be considered later. We made no attempt to de-

[1] J. Chem. Soc., **15**, 152 (1899).

termine its constitution, as it belongs in the field reserved by Dr. Fries.

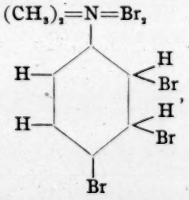
When the body containing 4 atoms of bromine was warmed with chloroform a viscous substance, having nearly the same composition, was produced, which had no action on potassic iodide and was converted, by sodic thiosulphate, into dibromdimethylaniline, it is probably, therefore, the benzdibromide of dimethylbromphenylamine hydrobromide,

$$Br_2C_6H_4BrN(CH_3)_2HBr,$$

and this view is confirmed by the facts that water or sodic hydrate gave with it dibromdimethylaniline, alcohol dibromdimethylaniline hydrobromide. This substance, on standing, acquired the property of acting on potassic iodide, which is caused by its passing into a red compound similar to that described above. We cannot understand, however, how such a body would be formed from $Br_4C_6H_4BrN(CH_3)_2HBr$.

The compound containing 6 atoms of bromine was made by adding bromine to the benz-3,4-dibromide of dimethylphenylamine dibromide. It was so unstable that we could not study it beyond determining its composition, but, from its relation to the other compounds described in this paper, there can be little doubt that it is the benztetrabromide of dimethylphenylamine dibromide, $Br_4C_6H_5N(CH_3)_2Br_2$.

The compound containing 5 atoms of bromine, obtained from the preceding by the removal of 1 molecule of hydrobromic acid, has already been proved to be different from Fries' perbromide, $C_6H_5Br_2N(CH_3)_2HBr_2$, and therefore it cannot be a perbromide at all, because this is the only one of this composition which contains 2 atoms of bromine acting upon potassic iodide. The only possible formula which we can find for it is the following,



so that it is the benzdibromide of dimethylparabromphenylamine dibromide. The para position of the substituted atom of bromine was established by the action of a strong solution of sodic thiosulphate (with potassic iodide), which converted it into parabromdimethylaniline.

The properties of the substance containing 5 atoms of bromine are in harmony with the formula just adopted. Alcohol in quantity or acetone alone (which gave a very violent action) formed the hydrobromide of dibromdimethylaniline, by the conversion of the benzdibromide into a brom compound and hydrobromic acid, which afterwards displaced the 2 atoms of bromine attached to the nitrogen. If the amount of alcohol used was small and the temperature did not rise above 50°, part of this bromine combined with the hydrobromide to give Fries' perbromide,

$$[C_6H_3Br_2N(CH_3)_2HBr]_2Br,$$

the melting-point of which we found at 133°, agreeing, as nearly as could be expected, with 135°, the temperature observed by Fries. The same perbromide seemed to be formed when the substance stood for some time in the air, or when it was treated, under proper conditions, with water, ligroin, or toluene.

Acetone, if diluted with chloroform, removed 2 atoms of bromine from the benzdibromide of dimethylparabromphenylamine dibromide, leaving an oily compound containing 3 atoms of bromine, which did not react with potassic iodide, with potassic hydrate gave dibromdimethylaniline, and with quinone a purplish-black color. These properties indicate that it is a benzdibromide of bromdimethylaniline,

$$Br_2C_6H_4BrN(CH_3)_2.$$

That it is not the hydrobromide of dibromdimethylaniline, which has the same composition, is shown by the reaction with quinone, and its easy solubility in acetone, in which the hydrobromide is nearly insoluble.

Unless there is some flaw in our reasoning, it is established beyond question that two of the substances just described are

amine dibromides. So far as we can find they belong to a new class of compounds, none of them being described in the chemical literature unless, indeed, a substance discovered by Raschig[1] should come here. One of the formulas he ascribes to it is $(CH_3)_2NBr_3.2H_2O$, which might be that of an amine dibromide, but, as it not only contains water of crystallization but is made with bromine water, whereas our amine dibromides all are decidedly unstable toward water, we think it probably belongs to a different series. On the other hand, there is no doubt that the compounds $(CH_3)_3NI_2$, discovered by Remsen and Norris,[2] and $(C_3H_7)_3NI_2$, discovered by Norris and Franklin,[3] belong to the same class as our amine dibromides. The compound $(CH_3)_3NICl$, made by Pictet and Krafft[4] may belong here also, although Norris,[5] on repeating their work most carefully, could not obtain this substance, but found that there was formed instead the $(CH_3)_3NI_2$ already mentioned. Dafert's[6] $C_6H_4NON(CH_3)_2I_2$ would be classed with our dibromides, but Bewad's[7] oxide, $(C_2H_5)_3NO$, which at first sight seems remotely related to our substances, can hardly be included with them, as it gives a hydrochloride.

In his work on the amine diiodides Norris used the action of strong sulphuric acid to distinguish between them and the periodides or perbromides which gave an effervescence of the halogen acid, whereas no gas was given off from the diiodides. We confirm this observation in the case of the parabromphenyldimethylamine diiodide, $C_6H_4BrN(CH_3)_2I_2$, melting-point 115°, made by us, but the test was, unfortunately, not applicable to our dibromides, as all of them were also benzdibromides, which give off hydrobromic acid when treated with sulphuric acid.

The two amine dibromides prepared by us show the follow-

[1] Ber. d. chem. Ges., **18**, 2250 (1885).

[2] THIS JOURNAL, **18**, 90 (1896). The compound $(CH_3)_3NBr_2$, mentioned in this preliminary paper, was proved, on more careful study, to be $(CH_3)_3NHBrBr$. Norris: THIS JOURNAL, **20**, 51 (1898).

[3] THIS JOURNAL, **21**, 499 (1899).

[4] Bull. Soc. Chim., [3], **7**, 74.

[5] THIS JOURNAL, **20**, 51 (1898).

[6] Monats. Chem., **4**, 496.

[7] J. d. Russ. Chem. Ges., **20**, 126. The existence of this substance was confirmed by Lachman, Ber. d. chem. Ges., **32**, 27.

ing characteristic properties: They are reddish-yellow, well-crystallized bodies, from which the 2 atoms of bromine are removed by potassic iodide, potassic hydrate, sodic acetate, sulphurous dioxide, acetone, or aniline, the free amine thus formed being more or less modified by secondary reactions. Alcohol, apparently, acts in the same way, but the amine is converted into the hydrobromide. Many attempts were made to replace the bromine by other radicals, but without success.

We have also studied the addition of bromine, in chloroform solution, to substituted dimethylanilines. With parabromdimethylaniline we could not obtain a direct addition of 2 atoms of bromine, but this compound, $Br_2C_6H_4BrN(CH_3)_2$, was probably obtained by the action of acetone, diluted with chloroform, on the benzdibromide of dimethylparaphenylamine dibromide, $Br_2C_6H_4BrN(CH_3)_2Br_2$. It was an oil, which, on standing, was gradually converted into the hydrobromide, $C_6H_3Br_2N(CH_3)_2HBr$. The product of the action of bromine on parabromdimethylaniline was the perbromide,

$$C_6H_3Br_2N(CH_3)_2HBr_2,$$

of Fries, not, however, absolutely pure, as it melted at 98° instead of 102°, and gave, with sodic acetate, some dibromdimethylaniline in addition to the normal product, tribrommethylaniline. The formation of this perbromide is to be expected, as probably the benzdibromide of the parabromdimethylaniline would be formed at first and our work indicates that this substance is very unstable, falling easily into dibromdimethylaniline and hydrobromic acid, which would combine to form the hydrobromide and this would then take up the 2 additional atoms of bromine.

The action of bromine on dibromdimethylaniline led only to a substance containing 6 atoms of bromine, compounds with less bromine could not be obtained. This compound gave up 2 atoms of bromine when treated with potassic iodide and sodic thiosulphate, but the organic product was tribrommethylaniline and, as 1 atom of bromine was used in the formation of this substance, it follows that there were really 3 atoms of active bromine. The compound is, therefore, probably the di-

bromdimethylaniline tetraperbromide, $C_6H_3Br_2N(CH_3)_2HBr_4$, and this view is supported by the facts that it gives hydrobromic acid with sulphuric acid and tribrommethylaniline hydrobromide, $C_6H_2Br_3N(CH_3)H_2Br$, with boiling alcohol or chloroform. As it, therefore, belongs in the field reserved by Dr. Fries we have made no extended study of it.

EXPERIMENTAL.

In order to prepare the addition-compounds described in this paper it was found necessary to purify the materials as follows: The dimethylaniline of the best quality, giving no violet coloration when treated with bleaching-powder, was redistilled, before it was used. The bromine was washed by shaking with water, dried with strong sulphuric acid and redistilled. This purification was necessary in preparing the addition-compounds, but not needed or used in making substitution-products. The chloroform used to dilute the reagents was of an excellent quality. It was dried carefully with calcic chloride and redistilled, after which it was kept in the dark.

Benz-3,4-dibromide of Dimethylaniline, $Br_2C_6H_5N(CH_3)_2$.—A solution of 16.3 grams of bromine, in 50 grams of chloroform, was added, slowly, to 12 grams of dimethylaniline, dissolved in 60 grams of chloroform, the liquid being thoroughly cooled with water during the process. At first the bromine was decolorized almost instantly, but toward the end of the addition the reddish tinge lingered for several minutes. In our first experiments we used more dilute solutions, containing only 10 per cent of the dimethylaniline, but we soon found that as good results could be obtained with 20, or even 30 per cent solutions if sufficient attention was paid to the cooling of the mixture. In any case the success of the operation depended on careful cooling, as, if the temperature was allowed to rise during the reaction, a tarry mass was left on evaporating off the chloroform, from which it was hard to obtain crystals.

After the addition was complete the chloroform was driven off either by distillation *in vacuo* or by passing a stream of dry air through the flask for some hours. The viscid, slightly yellow oil thus obtained usually solidified after standing for a

few days, forming long, yellowish plates, which, without further purification, were dried *in vacuo* and analyzed.

0.1559 gram substance gave, by the Carius method, 0.2098 gram AgBr.

	Calculated for $Br_2C_6H_5N(CH_3)_2$.	Found.
Br	56.94	57.24

Properties of Benz-3,4-dibromide of Dimethylaniline.—It usually crystallizes from chloroform in long, slightly yellow plates, but it appears sometimes in long, slender needles, arranged in radiating tufts; sometimes it was impossible to bring the viscous mass to crystallization. A specimen, after being washed with a small amount of chloroform, showed the melting-point 82°. This and the melting-points of similar compounds mentioned in this paper are only approximate numbers, as such unstable substances could not be recrystallized often enough to secure purity and, also, the melting was usually accompanied by decomposition, so that its temperature depended more or less on the conditions of the heating. The dibromide, when exposed to the air, is very slowly converted into parabromdimethylaniline, melting at 55°. It is soluble in ethyl or methyl alcohol, chloroform, or acetone; essentially insoluble in ether, benzene, toluene, ligroin, acetic ester or carbonic tetrachloride. It dissolves in dilute hydrochloric acid, nitric acid, or sulphuric acid, or in strong hydrochloric acid. Strong nitric acid dissolves it easily, but the solution soon turns yellow and then deposits a red oil and a red precipitate, which are soon converted into a yellow oil. Strong sulphuric acid causes an effervescence of hydrobromic acid and the solution soon becomes turbid.

It is decomposed very quickly by water and almost instantly by aqueous or alcoholic potassic hydrate, ammonic hydrate, or aniline, hydrobromic acid being removed with the formation of parabromdimethylaniline, which was purified either by distillation or crystallization from dilute alcohol, when it was identified by its melting-point,[1] 55°, and, for greater certainty, was analyzed:

[1] Würster and Beran: Ber. d. chem. Ges., **12**, 1820.

0.0420 gram substance gave 0.0398 gram AgBr.

	Calculated for $C_6H_4BrN(CH_3)_2$.	Found.
Br	40.00	40.31

The benz-3,4-dibromide of dimethylaniline adds bromine easily, giving the compounds described later in this paper. With potassic iodide and starch paste it gives no color reaction and with potassic iodide and sodic thiosulphate the product was parabromdimethylaniline. This reaction is mentioned because of its bearing on the results obtained with the substances containing more bromine. With quinone it gives a reddish-brown color.

Benz-3,4-dibromide of Dimethylethylphenylammonic Bromide, $Br_2C_6H_5N(CH_3)_2C_2H_5Br$.—The benzdibromide of dimethylaniline was treated with an excess of ethyl bromide, which at first converted it into an oil that did not mix with the excess of ethyl bromide, but after standing for a few minutes crystals began to appear on the surface of the oil and, after a few hours, it was almost completely converted into white, flat prisms mixed with a small amount of a red substance. These were dried on a porous plate and analyzed without further purification.

0.0663 gram substance gave 0.0955 gram AgBr.

	Calculated for $Br_2C_6H_5N(CH_3)_2C_2H_5Br$.	Found.
Br	61.54	61.27

The crystals are converted at once into a red oil by the addition of water.

The constitution of the benzdibromide of dimethylaniline is established by the experiments just described, as explained in the introduction.

Benz-3,4-dibromide of Dimethylphenylamine Dibromide, $Br_2C_6H_5N(CH_3)_2Br_2$.—To a solution of 12 grams of dimethylaniline, in 120 grams of chloroform, was added, slowly, a solution of 32 grams of bromine, in 100 grams of chloroform. The liquid was exposed to direct sunlight throughout the operation and was cooled with water during the addition of the first

half of the bromine, but as soon as the light yellow color of the mixture changed to red the cooling water was removed and the solution allowed to become hot from the heat of the reaction. The addition of the bromine usually took about half an hour and the product was then allowed to stand for an hour longer, after which the solution was evaporated by passing a stream of dry air through it, or better, by distillation *in vacuo*. The thick, red syrup thus obtained solidified, on standing, to a network of reddish needles, which were dried for analysis on a porous plate, in a desiccator, over soft paraffin and sulphuric acid. If the preparation ran properly no hydrobromic acid was given off in the course of it.

I. 0.2569 gram substance gave 0.4423 gram AgBr.
II. 0.1356 gram substance gave 0.2313 gram AgBr.

	Calculated for $Br_2C_6H_5N(CH_3)_2Br_2$.	Found. I.	II.
Br	72.56	73.21	72.61

When this substance was treated with potassic iodide and starch paste, a blue color showed that iodine was set free; accordingly, the amount of bromine which reacted with potassic iodide was determined as follows:[1] A weighed quantity of the substance was treated with 15 cc. of a solution containing 0.5 gram of potassic iodide and 20 cc. of a standard solution of sodic thiosulphate. After the crystals were entirely decomposed, the white, milky liquid was titrated with a standard solution of iodine, to determine how much thiosulphate remained undecomposed. By this method 0.0899 gram substance set free an amount of iodine corresponding to 0.0319 gram Br.

	Calculated for $Br_2C_6H_5N(CH_3)_2Br_2$.	Found.
Active Br_2	36.28	35.48

It follows from this that two of the atoms of bromine react with potassic iodide. If the experiment ran smoothly, the product should be parabromdimethylaniline, formed by the removal of the 2 atoms of active bromine and a molecule of hy-

[1] This method is founded on one in Sutton's "Volumetric Analysis," 7th Edition, p. 129.

drobromic acid ; as a matter of fact, the organic product of a similar experiment, obtained by extraction with ether, consisted principally of parabromdimethylaniline, but also contained a very small amount of dibromdimethylaniline.

Ethyl bromide dissolved the substance, but it crystallized out unchanged from this solution. The observations just described prove that the substance is the benz-3,4-dibromide of dimethylphenylamine dibromide, $Br_2C_6H_5N(CH_3)_2Br_2$, as explained in the introduction. This compound was also prepared by the action of more bromine on the benzdibromide of dimethylaniline, dissolved in chloroform.

Properties of the Benz-3,4-dibromide of Dimethylphenylamine Dibromide.—It forms long, yellowish-red needles, which appear red if seen in large masses. The melting-point was not sharp, as the melting usually took place at 65°–70°, but occasionally a specimen was obtained which melted at 68°. It is soluble in ethyl or methyl alcohol, chloroform, acetone, or ethyl acetate; somewhat soluble in tetrachloride of carbon ; essentially insoluble in benzene, toluene, or ligroin. All of these solvents, except chloroform and tetrachloride of carbon, react with the substance in the cold. It can be recrystallized from chloroform at ordinary temperatures, but if heated with it a reaction sets in. The various actions of these solvents are described later in the paper. Strong nitric acid dissolves it only partially and the mixture turns brown and turbid after a few minutes ; strong sulphuric acid dissolves it with evolution of hydrobromic acid. It is insoluble in dilute acids, whereas the benzdibromide of dimethylaniline dissolves in them. Aqueous or alcoholic potassic hydrate converts it into dibromdimethylaniline.

Action of Acetone on Benz-3,4-dibromide of Dimethylphenylamine Dibromide.—A strong solution of 1 gram of the substance, in chloroform, was treated, slowly, with acetone until it was decolorized. The solution was then warmed on the water-bath and the solvents removed by means of a current of dry air, after which the oily residue, that smelt distinctly of bromacetone, was allowed to stand *in vacuo* until this odor had dis-

appeared. Although it did not solidify so that the melting-point could be determined, we are of the opinion that it was the benz-3,4-dibromide of dimethylaniline, on account of the following reactions: Quinone gave the characteristic color and alkalies, or even water removed hydrobromic acid from it (detected by argentic nitrate) and formed parabromdimethylaniline, recognized by its odor, color reaction with quinone and melting-point, 55°.

Action of Ethyl Alcohol on Benz-3,4-dibromide of Dimethylphenylamine Dibromide.—When the substance was boiled with alcohol the solution was decolorized in a few minutes and the colorless liquid deposited, on evaporation, the hydrobromide of dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2HBr$, recognized by its melting-point, 110° (see later). Cold alcohol produced the same effect in 2–3 weeks; in this case the hydrobromide is deposited in beautiful, large, square plates.

Action of Benz-3,4-dibromide of Dimethylphenylamine Dibromide with Hot Chloroform.—One gram of the substance was boiled with 10 cc. of chloroform, on the water-bath, in a flask with a return-condenser, for 2 hours, at the end of which time the color of the solution had changed from red to yellow. A small amount of hydrobromic acid was given off, due probably to a secondary reaction; if the boiling was continued still longer, more hydrobromic acid was evolved and a red body, containing less bromine than the original substance, was formed; it, therefore, should not be continued beyond 2 hours. The yellow solution obtained in this time was freed from chloroform by warming it on the water-bath, in a current of dry air, when a yellowish oil was left, which we could not bring to solidification; it was, accordingly, dried *in vacuo* and analyzed. The two specimens analyzed proceeded from different preparations:

I. 0.1091 gram substance gave 0.1850 gram AgBr.
II. 0.1029 gram substance gave 0.1749 gram AgBr.

	Calculated for $C_8H_{11}NBr_4$.	Found. I.	II.
Br	72.56	72.18	72.35

The constancy in composition shown by these analyses indicates that the substance is a definite compound, in spite of its unsatisfactory physical properties, and also that it is isomeric, or nearly so, with the substance from which it was formed. It sets free no iodine from potassic iodide, but after standing for a few days it gains the power of doing this. Longer standing converts it into a red body, probably identical with that described in the next section. With alcohol, acetone, or acetic ester it yielded dibromdimethylaniline hydrobromide, melting-point 110°, while aqueous potassic hydrate gave dibromdimethylaniline. It is soluble in chloroform, but essentially insoluble in ether, toluene, or tetrachloride of carbon. Its most probable constitution is discussed in the introduction.

Decomposition of Benz-3,4-dibromide of Dimethylphenylamine Dibromide when Moistened with Chloroform.—When the substance, moistened with chloroform, was allowed to stand in a corked flask it slowly changed to a mass of brown-black plates. The formation of this dark substance was promoted by rubbing with a glass rod, or better still, by inoculation with some of the plates from a previous preparation. The dry dibromide also, sometimes, was converted spontaneously into this product, which then appeared as a reddish-black powder, but this action took place much more slowly than when the compound was moistened with chloroform. The substance was hard to obtain, as the change did not take place invariably and we have not succeeded in finding the conditions necessary to make certain of its preparation. It was dried in a desiccator, over soft paraffin and sulphuric acid:

0.1823 gram substance gave 0.3000 gram AgBr.

	Calculated for $C_{16}H_{24}N_2Br_7$.	Found.
Br	69.56	70.02

The substance sets free iodine from iodide of potassium, the amount of which was determined as follows:

0.1695 gram substance set free 0.0249 gram I.

	Calculated for $C_{16}H_{24}N_2Br_7$.	Found,
Br	9.96	9.19

That is, only one of the atoms of bromine can replace iodine in potassic iodide. These results and the brownish-black color, show that the body is a perbromide similar to those discovered by Fries,[1] and we therefore did not pursue the study of it. The sample analyzed melted at 105°.

Dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2$.—This substance was frequently obtained in the course of our work on the benz-3,4-dibromide of dimethylphenylamine dibromide. It was most conveniently made from the oil left after evaporating off the chloroform in the preparation of this body. This oil was treated with an aqueous solution of potassic hydrate, the product extracted with ether and, after distilling off the ether, the residue was dried and distilled under ordinary pressure. Care should be taken that a sufficient amount of potassic hydrate was used, as the presence of dibromdimethylaniline hydrobromide produced explosions during the distillation. Parabromdimethylaniline boils at about the same temperature (264°) as the dibrom compound; it is wise, therefore, to use enough bromine in the preparation of the original oil to make certain that all the benzdibromide of dimethylaniline should take up at least two more atoms of bromine. If parabromdimethylaniline was found to be present in the product, it could be removed, in great measure, by allowing the mixture to stand for 2 or 3 weeks, when most of the monobrom compound crystallized out. The yield of dibromdimethylaniline was very good, averaging 85–95 per cent of the theory.

0.3532 gram substance gave 0.4777 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2$.	Found.
Br	57.34	57.55

Properties of Dibromdimethylaniline.—We found the boiling-point of this liquid 264°, at 760 mm. This is somewhat lower than the boiling-point 275°, at 746 mm., found by Fries[1] for his *o,p*-dibromdimethylaniline, but we feel no doubt in regard to the identity of the two compounds, as Fries purified his product by conversion into the tin salt, whereas ours was only

[1] Ber. d. chem. Ges., **37**, 2338 (1904).

submitted to distillation and, therefore, the lower boiling-point found by us is undoubtedly due to a quantity of impurity too small to be shown by our analysis. His boiling-point should be adopted as the correct one. It is a colorless, oily liquid, which mixes with ethyl or methyl alcohol, ether, benzene, toluene, chloroform, acetone, or ethyl acetate, but not with water. It is soluble in moderately strong acids, takes up bromine to form a compound described later, combines with methyl iodide or ethyl bromide to form ammonium compounds, and gives a violet color with quinone.

Hydrobromide of Dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2HBr$.—This substance appeared frequently as a decomposition-product of the addition-compounds described in this paper. It can be made easily as follows: The benz-3,4-dibromide of dimethylphenylamine dibromide, which can be used in the viscous state, as first obtained, was treated with dilute alcoholic potassic hydrate, in small portions at a time, until the color was just discharged; the potassic bromide was then filtered out and the alcoholic filtrate evaporated on the water-bath until the product began to crystallize. It was also made by passing dry hydrobromic acid into a solution of dibromdimethylaniline, when it appeared as a white precipitate. It was purified by recrystallization once from alcohol and several times from acetone, until it showed the constant melting-point 110°, when it was dried *in vacuo* and analyzed:

I. 0.1011 gram substance gave 0.1594 gram AgBr.
II. 0.2137 gram substance gave 0.3355 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBr$.	Found. I.	II.
Br	66.66	67.07	66.80

Properties of Dibromdimethylaniline Hydrobromide.—It crystallizes from alcohol in colorless, square plates; from chloroform in cubes modified by many other planes; from acetone in cubical forms, often with hollows in the sides, as in some crystals of salt. It melts at 110° to a clear, colorless liquid and, if heated to 140°, is suddenly converted into a blue coloring-matter. It is soluble in alcohol or chloroform; fairly soluble in warm ether, nearly insoluble in cold; very slightly

soluble in acetone ; essentially insoluble in benzene, toluene, acetic ester, or carbonic tetrachloride. The strong mineral acids dissolve it easily. An alkali or even water decomposes it at once, dibromdimethylaniline being formed, but it can be boiled with alcohol for several hours without decomposition.

Benztetrabromide of Dimethylphenylamine Dibromide, $Br_4C_6H_5N(CH_3)_2Br_2$.—This substance, which contained more bromine than any other prepared by us, was obtained with difficulty because of its strong tendency to lose hydrobromic acid and form the benzdibromide of dimethylbromphenylamine dibromide, which is described later. The body containing 6 atoms of bromine was prepared as follows : A solution of 4.8 grams of bromine, in 24 grams of chloroform, was added, slowly, to a solution of 1.2 grams of dimethylaniline in 6 grams of chloroform, the mixture was cooled from the first with ice-water and exposed to direct sunlight. The red solution thus obtained was allowed to stand for more than 2 days, at ordinary temperatures, after which the chloroform was distilled off *in vacuo* and the thick, red liquid thus obtained deposited small, reddish crystals of the substance, after standing a few minutes.

0.1286 gram substance gave 0.2386 gram AgBr.

	Calculated for $Br_4C_6H_5N(CH_3)_2Br_2$.	Found.
Br	79.86	78.96

The compound appears in small, reddish needles and is very unstable, splitting off hydrobromic acid to form the body with 5 atoms of bromine (described next) so that the hexabrom compound usually was not the product of the preparation described above, but was obtained only when the utmost care was exercised to exclude every trace of moisture. It also gives off 1 molecule of hydrobromic acid when heated, so no attempt was made to determine its melting-point.

Benzdibromide of Dimethylbromphenylamine Dibromide, $Br_2C_6H_4BrN(CH_3)_2Br_2$.—The method for preparing this substance was essentially the same as that given for the preceding compound, except that no extraordinary precautions were

taken. We used 12 grams of dimethylaniline, dissolved in 120 grams of chloroform, and 48 grams of bromine, dissolved in 120 grams of chloroform. The solution of bromine was added slowly to that of the dimethylaniline, the mixture being cooled with ice-water during the addition of the first third of the bromine, as otherwise the reaction became too violent. After that the remainder of the bromine was added without cooling and the mixture finally warmed on the water-bath, for 2 hours. We carried on our earlier preparations in sunlight, but later experiments showed that this was unnecessary. The reddish liquid thus obtained was freed from chloroform by distillation, at first at ordinary pressure, finally *in vacuo*, and the thick, oily residue allowed to stand, at ordinary temperatures, for 2–3 days, when it solidified to a mass of large crystals. These were dried for analysis, first on a porous plate, later in a desiccator over soft paraffin :

I. 0.3674 gram substance gave 0.6636 gram AgBr.
II. 0.1861 gram substance gave 0.3345 gram AgBr.

	Calculated for $C_6H_4Br_3N(CH_3)_2Br_2$.	Found. I.	II.
Br	76.92	76.85	76.52

0.6675 gram substance gave with KI and $Na_2S_2O_3$ 0.1960 gram active Br.

	Calculated for $C_6H_4Br_3N(CH_3)_2Br_2$.	Found.
2Br	30.77	29.33

Properties of the Benzdibromide of Dimethylbromphenylamine Dibromide.—It forms large, well-formed, long, reddish prisms, terminated by a single plane at an oblique angle. Smaller crystals are yellow. On standing in the air it slowly turns to a reddish-black powder. It melts at 78°, but when the melted substance is heated to a higher temperature it begins to decompose, giving off white fumes which condense on the upper part of the tube to a colorless liquid, soon crystallizing in needles. The residue left in the bottom of the tube has a violet color. Neither of these substances was studied further. It seems not to be decomposed by chloroform, in which it is soluble, or tetrachloride of carbon, in which it is very slightly

soluble, but all other solvents tried decomposed it in the ways described later in this paper. When heated with water, it turns black, forming, probably, the same product as with air. Strong hydrochloric acid dissolves it, apparently unchanged; strong nitric acid dissolves it, forming a yellow solution which soon grows brown and turbid; strong sulphuric acid partially dissolves it with an effervescence of hydrobromic acid. Aqueous or alcoholic potassic hydrate converts it into dibromdimethylaniline. When the substance is fused for several minutes with symmetrical tribromaniline a red body is formed; fusion with quinone gives a red, with pyrocatechin a brown and with tetrabrompyrocatechin a red product; none of these reagents act on it in solution and as these products seemed to be due to a decomposition of the substance we did not pursue this part of the research further.

Action of Acetone on the Benzdibromide of Dimethylbromphenylamine Dibromide.—Acetone acted so violently on this substance that the product was a black, tarry mass, the formation of which was accompanied by that of bromacetone, to judge from the effect on the eyes. The tar, after standing 2–3 weeks, deposited well-formed, square crystals of dibromdimethylaniline hydrobromide, recognized by its melting-point, 110°, and some dibromdimethylaniline was detected in the pasty mass in which the crystals were embedded.

If, instead of using pure acetone, it was used diluted with chloroform, a different result was obtained. One gram of benzdibromide of dimethylbromphenylamine dibromide was dissolved in 10 cc. of chloroform and acetone added in small portions at a time, with vigorous shaking between each addition, until the solution was decolorized. The liquid was then concentrated on the water-bath to a volume of about 3 cc. and the drying was finished *in vacuo* over glycerol, which, in 1 night, removed the odor of the bromacetone. As the residue refused to solidify, it was analyzed as it stood. The two analyses were made with different preparations:

I. 0.0912 gram substance gave 0.1396 gram AgBr.
II. 0.1435 gram substance gave 0.2195 gram AgBr.

	Calculated for $Br_2C_6H_4BrN(CH_3)_2$.	Found. I.	II.
Br	66.66	65.12	65.06

These results are as near as could be expected from such a body. It is an oil, which had a dark color, as obtained by us, but is probably colorless when pure. It mixes freely with acetone, gives no reaction with potassic iodide and starch, but a purplish-black color with quinone. Aqueous potassic hydrate converts it into dibromdimethylaniline, with loss of hydrobromic acid. These properties show that it is probably the benzdibromide of bromdimethylaniline, $Br_2C_6H_4BrN(CH_3)_2$, as explained in the introduction. It is isomeric with the dibromdimethylaniline hydrobromide, $C_6H_3Br_2N(CH_3)_2HBr$, into which it is converted after standing for several days.

Action of Alcohol on the Benzdibromide of Dimethylbromphenylamine Dibromide.—If the substance was boiled with alcohol for some minutes the red color was discharged and dibromdimethylaniline hydrobromide was formed; the same reaction took place when it was allowed to stand several weeks, with an excess of alcohol, at ordinary temperatures, but a different result was obtained when it was heated to 50° with just enough alcohol to dissolve it, then, on cooling, a voluminous precipitate of glistening black plates was deposited. The same substance appeared in the form of large, black prisms, when a cold, concentrated alcoholic solution was allowed to evaporate spontaneously; the prisms began to form in 2–5 hours, were at their best in 12–20 hours, and began to decompose after 24 hours. It was dried, for analysis, on a porous plate in a desiccator:

I. 0.0744 gram substance gave 0.1235 gram AgBr.
II. 0.2112 gram substance gave 0.3495 gram AgBr.

	Calculated for $C_{16}H_{20}N_2Br_4$.	Found. I.	II.
Br	70.00	70.61	70.42

The amount of bromine which can set free iodine from potassic iodide was determined:

0.3492 gram substance gave 0.0374 gram Br.

	Calculated for $C_{16}H_{20}N_2Br_7$.	Found.
Br_1	11.43	10.70

The amount of hydrobromic acid was also determined which was removed from the body by the action of water, the secondary product being dibromdimethylaniline:

0.1207 gram substance gave 0.0851 gram AgBr.

	Calculated for $C_{16}H_{20}N_2Br_7$.	Found.
Br_3	30.00	30.00

These data show that the substance is a perbromide and, as it melted at 133°, it is probably identical with Fries'

$$[C_6H_3Br_2N(CH_3)_2HBr]_2Br,$$

which melts at 135°.

Toluene, when shaken for 40 hours with the benzdibromide of dimethylbromphenylamine dibromide, converts it into the perbromide melting at 133°, described above, and ligroin has the same effect when allowed to stand with it. In each case the liquid takes up bromine.

Action of Aniline on Benzdibromide of Dimethylbromphenylamine Dibromide.—The principal products of this reaction were aniline hydrobromide and dibromdimethylaniline, whether the reagents were dissolved in chloroform or mixed undiluted. In the latter case, in 3 experiments out of 10 or more tried by us, we obtained small quantities of red crystals, amounting to not more than 1 per cent of the dibromide used. As we could not find the conditions under which these crystals were formed, this part of the work was abandoned. They may be analogous to the benzidine compound observed by Fries.

Action of Potassic Iodide on Benzdibromide of Dimethylparabromphenylamine Dibromide.—This reaction was of importance, as on it was founded one of our methods of analysis. A dilute solution of potassic iodide, when mixed with our compound, at once developed a reddish color from the iodine set free, as was proved by the reaction with starch paste. If the amount of free iodine was determined at once, with sodic thiosulphate,

constant results were obtained, but if the mixture containing the free iodine was allowed to stand, it was found that it gradually went into combination again, so, to get good results from this analytical process, the potassic iodide should be added mixed with a known excess of thiosulphate, and the amount of thiosulphate, remaining after the action, determined.

The organic product of the action of potassic iodide and sodic thiosulphate was determined by the following experiment: Three grams of benzdibromide of dimethylbromphenylamine dibromide were added to a solution of 10 grams of potassic iodide and 10 grams of sodic thiosulphate, in 200 cc. of water. The mixture was shaken thoroughly and allowed to stand for 2 hours, after which it was extracted with ether. The extract distilled over at 264° and had the odor of dibromdimethylaniline; it also gave the characteristic color with quinone. For greater certainty it was analyzed:

0.2941 gram substance gave 0.3919 gram AgBr.

	Calculated for $C_4H_3Br_2N(CH_3)_2$.	Found.
Br	57.34	56.72

The aqueous solution, left after the extraction with ether, contained no sulphur and did not smell of sulphurous dioxide.

When a much stronger solution of the iodide and thiosulphate was used, a precipitate of sulphur was formed soon after the materials were mixed and there was a strong odor of sulphurous dioxide. The ether extract, in this case, consisted of much parabromdimethylaniline mixed with less dibromdimethylaniline. The parabrom compound was evidently formed by the direct removal of all the added bromine by the reducing agent. The bearing of this experiment on the constitution of the substance is discussed in the introduction.

If a solution of benzdibromide of dimethylparabromphenylamine dibromide, in chloroform, was treated with solid potassic iodide, a new substance was formed crystallizing in reddish-yellow, flat prisms, with square ends and melting at 137°. This compound was prepared as follows: The concentrated chloroform solution of the dibromide, obtained in its prepara-

tion by evaporating off the excess of chloroform, was used. To this was added one-fourth of its weight of pulverized potassic iodide and, after a few minutes, twice its volume of alcohol. After standing for 10 minutes the mixture was treated with distilled water, which was added, drop by drop, on the edge of the beaker, until the dirty brown precipitate formed at first just dissolved on shaking. The liquid was then decanted as quickly as possible from the solid potassic iodide and in 1–2 minutes it became nearly solid, from the deposition of a network of beautiful, reddish-yellow needles. The beaker was allowed to stand several minutes, to secure complete precipitation, and then the solid was filtered out and recrystallized from alcohol until it showed the constant melting-point 137°.

0.1724 gram substance gave, on combustion, 0.1251 gram CO_2 and 0.0425 gram H_2O.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBrI$.	Found.
C	19.72	19.79
H	2.05	2.74

0.1615 gram substance, treated with sodic thiosulphate and potassic iodide, showed 0.0374 gram active I.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBrI$.	Found.
I	26.33	23.16

This result, although not very exact, shows that the atom of iodine was loosely attached. Quinone or ethyl bromide had no effect on it; aqueous potassic hydrate gave dibromdimethylaniline. From these observations it can be inferred that the iodine is attached to the bromine of a hydrobromide; the substance, therefore, belongs to the same class as the perbromides and falls outside of the field of our research. It seems evident that the loss of free iodine observed in our analytical work on amine dibromides, when the iodine was allowed to stand with the amine, was due to the formation of a compound similar to this.

Action of Sodic Acetate on Benzdibromide of Dimethylparabromphenylamine Dibromide.—Pulverized, anhydrous sodic acetate was added to a solution of 1 gram of the dibromide, in 10

cc. of glacial acetic acid, until the color was completely discharged. The solution was then neutralized with dilute sodic hydrate and extracted with ether. The extract was an oil, which had the odor of dibromdimethylaniline and gave, with quinone, the proper color reaction. Its identity was established by treating it with gaseous hydrobromic acid, which converted it into the hydrobromide, $C_6H_3Br_2N(CH_3)_2HBr$, melting at 110°.

The Addition of Bromine to Parabromdimethylaniline. — A number of attempts to obtain a product formed by the addition of 2 atoms of bromine to parabromdimethylaniline led to no favorable result. Usually a red substance was formed, probably Fries' $[C_6H_3Br_2N(CH_3)_2HBr]_2Br$, or else the following compound, containing 5 atoms of bromine, was formed, and part of the parabromdimethylaniline remained unaltered. On one occasion we thought we obtained the desired substance, but the amount was too small to identify it with certainty. Although this substance could not be made directly from parabromdimethylaniline, we probably obtained it, as already stated, by the action of acetone, diluted with chloroform, on the benzdibromide of dimethylparabromphenylamine dibromide.

A substance containing 5 atoms of bromine was obtained, without difficulty, by adding 16 grams of bromine, dissolved in 100 grams of chloroform, to 10 grams of parabromdimethylaniline, dissolved in 100 grams of chloroform ; on evaporation *in vacuo* the substance was obtained in slender, reddish-brown prisms, which melted at 98°.

0.1643 gram substance gave 0.2989 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBr_3$.	Found.
Br	76.92	77.43

This substance is, without doubt, principally Fries' dibromdimethylaniline perbromide, which melts at 102° and corresponds to it in its other properties. The somewhat lower melting-point of our preparation indicates, however, that it was not perfectly pure and this is confirmed by the fact that sodic acetate gave some dibromdimethylaniline with our specimen, in

addition to the tribrommethylaniline which is the normal product with Fries' compound. That his substance would be the most probable product in this case is explained in the introduction.

The Addition of Bromine to Dibromdimethylaniline.—All our attempts to prepare a compound containing 4 atoms of bromine in this case led to no result, but one containing 6 atoms of bromine was prepared as follows: Six and four-tenths grams of bromine, dissolved in 30 grams of chloroform, were added, slowly, to 5.6 grams of dibromdimethylaniline, dissolved in 50 grams of chloroform. The bromine was decolorized almost as fast as it was added and little heat was evolved. On standing over night the new compound crystallized out in reddish prisms, which were dried *in vacuo* for analysis:

0.3050 gram substance gave 0.5695 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBr_4$.	Found.
Br	80.00	79.45

0.5551 gram substance contained 0.1589 gram active Br.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBr_4$.	Found.
2Br	26.67	28.64

This result seems, at first sight, to indicate that the substance contains 2 atoms of active bromine, but, as the organic product is tribrommethylaniline, 1 atom of bromine has been used up in making this substance and, in fact, there are 3 atoms of active bromine. The substance, therefore, is probably a perbromide, $C_6H_3Br_2N(CH_3)_2HBr_4$, of a different class from any of those obtained by Fries from dimethylaniline. This inference is supported by its properties. It crystallizes in yellowish-red, flat prisms, so small that they look like needles, melting at 98°. Strong sulphuric acid causes an effervescence, which consists, in part, of hydrobromic acid. Boiling alcohol or chloroform converted it into tribrommethylaniline hydrobromide, $C_6H_2Br_3NHCH_3HBr$, which is described below. Acetone gave the hydrobromide of dibromdimethylaniline, recognized by its melting-point, 110°. Potassic hydrate gave dibromdimethylaniline. With cold alcohol it

formed Fries' perbromide, $[C_6H_3Br_2N(CH_3)_2HBr]_2Br$, melting at 135°.

Hydrobromide of Tribrommethylaniline, $C_6H_2Br_3NHCH_3HBr$.—Three grams of the dibromdimethylaniline tetraperbromide, mentioned above, were boiled, on the water-bath, with 30 cc. of alcohol, until the red color had disappeared. The colorless solution, on cooling, deposited a white crystalline precipitate, which, after washing with a little chloroform and 2 or 3 recrystallizations from that solvent, appeared in cubes or closely related forms. It turned brown at about 200° and melted at 202° to a black liquid.

I. 0.2133 gram substance gave 0.3744 gram AgBr.
II. 0.1253 gram substance gave 0.2244 gram AgBr.

	Calculated for $C_6H_2Br_3NHCH_3HBr$.	Found. I.	II.
Br	75.46	74.71	76.21

That it is the hydrobromide of tribrommethylaniline was proved by treating it with water, which decomposed it into hydrobromic acid and tribrommethylaniline, $C_6H_2Br_3NHCH_3$, recognized by its melting-point,[1] 37°. With the hydrobromide of tribrommethylaniline some dibromdimethylaniline was also formed, which was removed by the crystallization from chloroform. Boiling chloroform also gave the hydrobromide.

Properties of the Hydrobromide of Tribrommethylaniline, $C_6H_2Br_3NHCH_3HBr$.—It crystallizes in white cubes or in similar forms, modified by many planes. It turns brown at 200° and melts, to a black liquid, at 202°. It is somewhat soluble in acetone or hot chloroform; nearly insoluble in benzene, toluene, ethyl acetate, or carbonic tetrachloride. Its behavior with water has been mentioned already.

Parabromphenyldimethylamine Diiodide, $C_6H_4BrN(CH_3)_2I_2$.—This compound was made by adding a hot solution of 2.6 grams of iodine, in 25 grams of chloroform, to 2 grams of parabromdimethylaniline, dissolved in 10 grams of chloroform. The almost black mixture deposited crystals of the new com-

[1] Fries: Ber. d. chem. Ges., **37**, 2338 (1904).

pound as it cooled. These were dried on a tile, in a desiccator, for analysis:

0.2521 gram substance gave 0.3736 gram AgBr + AgI.

	Calculated for $C_6H_4BrN(CH_3)_2I_2$.	Found.
Br + I	73.55	75.21

This result, bad as it is, shows the substance can have no other formula.

0.2102 gram substance lost 0.1154 gram I when treated with $Na_2S_2O_3$ and KI.

	Calculated for $C_6H_4BrN(CH_3)_2I_2$.	Found.
I_2	55.94	54.91

Properties of the Parabromphenyldimethylamine Diiodide.—It forms black, flat prisms, melting at 115°. It is slightly soluble in alcohol, acetone, or acetic ester, giving green solutions; benzene, toluene, ligroin, or carbonic tetrachloride does not dissolve it, but the solvent slowly takes on a reddish color from the removal of a part of the iodine from the compound. An aqueous solution of potassic iodide removes a considerable amount of iodine, as was shown by the starch paste test. Ethyl bromide has no action upon the compound. Strong sulphuric acid gives no effervescence with it. A number of attempts to replace the iodine with other radicals led to no successful result.

CAMBRIDGE, MASS.,
May 4, 1904.

POSTSCRIPT.—Two months after the manuscript of the foregoing paper had been sent to the editor of this JOURNAL, that is on July 3rd, we received a paper by A. Hantzsch and W. Graf[1] on the same subject, in which they describe the dimethylparabromphenylamine dibromide, $C_6H_4BrN(CH_3)_2Br_2$, prepared by them, without difficulty, from parabromdimethylaniline, whereas, of the many experiments of this sort tried by us only one gave this product, and that not in quantity sufficient for identification. On the other hand, they were unable

[1] Ber. d. chem. Ges., 38, 2154 (1905).

to obtain stable addition-compounds of unsubstituted dimethylaniline under any conditions, whereas we had no trouble in preparing the di-, tetra- and hexabromide described above. Oddly enough, therefore, the two papers supplement each other, and together give a nearly complete account of these compounds. The nature of the slight differences in procedure which led to these different results can be only a matter of conjecture at present.

The sketch of the history of the subject given in our paper should be modified according to the newer work in the paper of Hantzsch and Graf.

August 18, 1905.

THE APPROXIMATE COMPOSITION OF THE HYDRATES FORMED BY A NUMBER OF ELECTROLYTES IN AQUEOUS SOLUTIONS; TOGETHER WITH A BRIEF GENERAL DISCUSSION OF THE RESULTS THUS FAR OBTAINED.

[THIRTEENTH PAPER.]

This investigation, like the preceding eight in this field, was carried out under a grant from the Carnegie Institution.

By Harry C. Jones and H. P. Bassett.

A number of lines of evidence bearing upon the question of dissolved substances combining with the solvent, have been considered in preceding papers. Certain comparatively new lines will be taken up in this one. Dr. G. N. Lewis, of Harvard, called my attention to various color changes that seem to have a direct bearing upon the problem in question. He has informed me, by private letter from the Government Laboratories in the Philippines, where he is now stationed, that his own observations will soon be published in the *Zeitschrift für physikalische Chemie*, and has kindly permitted me to refer to them in advance. The experiments described below consist of modi-

fications of the reactions pointed out by Dr. Lewis, together with a number of additional color changes.

When cobalt chloride, with its 6 molecules of water of crystallization, is dehydrated, either wholly or in part, there is, as is well known, a marked color change from the typical reddish color of the solution to a beautiful blue. This change in color can be readily effected, in solution, by a number of substances. The fact has long been known, but its bearing on the theory of hydrates in solution, as advocated by Jones, has been pointed out only once, and that in a recent[1] paper by this author.

If, to a fairly concentrated solution of cobalt chloride, a comparatively small amount of fused calcium chloride is added, the blue color quickly makes its appearance. Since the earlier investigations of Jones and Getman[2] have shown that aluminium chloride has even greater hydrating power than calcium chloride, we should expect a smaller quantity of aluminium chloride to effect the same color change. Such is the fact.

If crystallized calcium chloride is added to a fairly concentrated solution of cobalt chloride, the blue color does not appear at first, but after adding a large amount of the crystallized salt and vigorously shaking, the blue color gradually appears and finally becomes quite intense. This shows beyond question, to our minds, that calcium chloride, with 6 molecules of water of crystallization, can, in solution, combine with a still larger quantity of water, as is demonstrated by a partial dehydration of the cobalt chloride and the consequent blue color.

About the only reasonable objection that could be offered to our conclusion from this experiment is that, in the above cases, there is a double chloride formed which has a blue color. The number of lines of evidence against this conclusion is so large as to render it entirely untenable. In the first place, it was shown some years ago by Jones and Ota[3] and by Jones and Knight[4] that double chlorides, even in concentrated solutions, could not exist, to any great extent, as such, but break down

[1] J. Chim. Phys., **3**, 455 (1905);
[2] Z. physik. Chem., **49**, 385 (1904).
[3] THIS JOURNAL, **22**, 5 (1899).
[4] *Ibid.*, **22**, 110 (1899).

into the constituent chlorides. In the light of these facts it is impossible to conceive of sufficient double chloride existing in the solutions, to give them a pure blue color in the presence of the red cobalt chloride, even if a blue double chloride were formed.

Again, the same reaction can be effected by adding concentrated hydrochloric acid to a concentrated solution of cobalt chloride, while no amount of the dilute acid will change the solution of the cobalt salt to a blue color. This cannot be due to the formation of a double compound with the hydrochloric acid, for the reasons already given for the salts.

The above color change of the solution of cobalt chloride from red to blue can also be effected by phosphorus pentoxide. When this dissolves an acid is formed, but the acid is so weak, relative to hydrochloric acid, that the amount of hydrochloric acid set free would be far less than in an ordinarily dilute solution of hydrochloric acid. The color change is effected by the phosphorus pentoxide, but not by dilute hydrochloric acid.

Taking into account the above and many other facts bearing upon the problem, it seems that any attempt to account for these color changes on the basis of the formation of double compounds must be regarded as untenable.

We have here, then, a well-defined example of hydration taking place in solution. In the case of crystallized calcium chloride, the change in color of the cobalt chloride demonstrates that the calcium chloride can and does combine with more water in solution than it can bring with it out of solution, as water of crystallization, which is the point to be proved.

If, to any of the cobalt solutions mentioned above, water be added, the blue color immediately disappears and the characteristic red color of the cobalt salt again makes its appearance. This is, of course, exactly in conformity with our conception that these experiments illustrate dehydration even in aqueous solutions.

Color reactions similar to the above can be effected with cupric bromide. When salts with large hydrating power are added to dilute solutions of cupric bromide, which are blue, a

part of the water is removed from the cupric salt and the blue color gives way to the greenish, or greenish-brown, that is characteristic of concentrated, or only partially hydrated solutions of cupric bromide.

These reactions will not be referred to in any further detail in this connection, since they are now being studied quantitatively by means of the spectroscope.

The Effect of Temperature on Water of Crystallization, as Bearing on the Theory of Hydrates in Solution.

Another line of evidence, which seems to us to have some bearing, at least indirectly, on the question as to whether there is combination between the solvent and dissolved substances is the following: If dissolved substances combine with the solvent, we know that the resulting compounds are unstable, especially at elevated temperatures. That this is the case is shown by the fact that most of the water can readily be driven off from solutions of salts at the boiling-points of these solutions. Indeed, in most cases, practically all the water can be thus removed, except that which is held in combination by the salt at the temperature in question, as water of crystallization. We have already shown that salts which crystallize with water of crystallization can combine, when in solution, at ordinary temperatures, with a much larger amount of water than they can bring with them out of solution, when they crystallize. These hydrates are, then, more stable the lower the temperature and, in terms of our hydrate theory, we should expect that *a salt would be able to bring with it out of solution more water, as water of crystallization, the lower the temperature at which the crystals were formed.*

We were surprised, on examining the literature, to find how large an amount of evidence was available, bearing on this point. A good many cases are well known, but we found on record an unexpectedly large number of salts that have already been shown to crystallize with varying amounts of water, depending upon the temperature at which the crystals were formed. A few examples are given to bring out the general relation, that *the number of molecules of water of crystal-*

lization is greater the lower the temperature at which the salt is crystallized.

Salt.	Water of crystallization.	Temperature of crystallization.
$LiCl$	$2H_2O$	12°.5
"	$3H_2O$	—15°
$LiBr$	H_2O	
"	$2H_2O$	Not stable above 4°
"	$3H_2O$	—40°
$LiNO_3$	Anhydrous	15°
"	$5H_2O$	Below 10°
$NaBr$	Anhydrous	Hot, concentrated solution
"	$2H_2O$	Ordinary temperatures
NaI	Anhydrous	Hot, concentrated solution
"	$2H_2O$	Ordinary temperatures
Na_2CO_3	$7H_2O$	Warm, saturated solution
"	$10H_2O$	Ordinary temperatures
$CaCl_2$	H_2O	As the temperature of crystallization is lower and lower
"	$2H_2O$	
"	$4H_2O$	
"	$6H_2O$	
$Sr(NO_3)_2$	Anhydrous	Above 16°.8
"	$4H_2O$	Below 16°.8
$MgCl_2$	$6H_2O$	Elevated temperatures
"	$8H_2O$	Above 20°
"	$10H_2O$	20°
"	$12H_2O$	—10° to —12°
$MgBr_2$	$4H_2O$	11°.5 to 12°.5
"	$6H_2O$	
"	$10H_2O$	—16°
$Mg(NO_3)_2$	$2H_2O$	Elevated temperatures
"	$6H_2O$	18°
"	$9H_2O$	—17°
$ZnCl_2$	H_2O	Elevated temperatures
"	$2H_2O$	
"	$3H_2O$	—21°
$ZnBr_2$	Anhydrous	35°
"	$2H_2O$	—8°
"	$3H_2O$	—15°
$Zn(NO_3)_2$	$3H_2O$	36°

Salt.	Water of crystallization.	Temperature of crystallization.
$Zn(NO_3)_2$	$6H_2O$	From concentrated solution
"	$9H_2O$	—18°
$Cd(NO_3)_2$	$4H_2O$	Ordinary temperatures
"	$9H_2O$	10° to —16°
$CdSO_4$	H_2O	103° to 104°
"	$7H_2O$	—20°
"	$9H_2O$	Very low temperatures
$MnCl_2$	$2H_2O$	20°
"	$4H_2O$	15°
"	$6H_2O$	—21°
"	$11H_2O$	—21° to —37°
"	$12H_2O$	—48°
MnI_2	$4H_2O$	0° to —2°.7
"	$6H_2O$	—5°
"	$9H_2O$	—20°
$MnSO_4$	$3H_2O$	25° to 31°, as a crust
"	$4H_2O$	25° to 31°
"	$5H_2O$	15° to 20°
"	$7H_2O$	0° or below 6°
$Ni(NO_3)_2$	$3H_2O$	58° and above
"	$6H_2O$	—16°
"	$9H_2O$	—27°
$Co(NO_3)_2$	$3H_2O$	56° to 91°
"	$6H_2O$	—22° to 56°
"	$9H_2O$	—29° to —22°
$Cu(NO_3)_2$	$3H_2O$	At ordinary temperatures
"	$6H_2O$	About 0° to —10°
"	$9H_2O$	—20° to —24°
$AlCl_3$	$6H_2O$	2° to 20°
"	$9H_2O$	—8° to 2°
$AlBr_3$	$9H_2O$	Ordinary temperatures
"	$15H_2O$	—10° to —18°
AlI_3	$6H_2O$	Ordinary temperatures
"	$15H_2O$	—18°
$Fe(NO_3)_2$	$6H_2O$	—9°
"	$9H_2O$	—27°
$FeCl_3$	Anhydrous	80° and above
"	$2H_2O$	60° to 80

Salt.	Water of crystallization.	Temperature of crystallization.
$FeCl_3$	$2\frac{1}{2}H_2O$	40° to 60°
"	$3\frac{1}{2}H_2O$	20°
"	$6H_2O$	20° to —16°

While there is a much larger number of cases on record where water of crystallization varies with the temperature, in many of them the temperatures at which the different amounts of water of crystallization were obtained are either not given at all, or are given only approximately. Such cases, in their present state, are of comparatively little value as bearing on the problem under discussion.

The examples given above suffice to show the general nature of the relation between water of crystallization and the temperature at which the salt was crystallized. Work is now in progress on this point and we hope to find even a larger number of instances where temperature affects water of crystallization and, if possible, to establish even more marked effects of temperature on the amount of water with which the salt crystallizes.

It might be concluded that these facts are at variance with the relation, pointed out by Jones and Getman,[1] between water of crystallization and lowering of freezing-point. This is not the case because the amounts of water of crystallization, as taken by Jones and Getman, are the quantities with which the salts ordinarily crystallize, *i. e.*, under as nearly comparable conditions of temperature as possible. These facts, then, have no direct bearing on the above relation, which is regarded as strong evidence in support of our hydrate conception.

Aim of the Present Investigation.

The aim of the present investigation is to determine, as closely as possible, the composition of the hydrates formed by a number of familiar salts, acids and bases, at different concentrations. The methods employed are similar to those used

[1] THIS JOURNAL, 31, 344. Z. physik. Chem., 49, 433 (1904). J. Chim. Phys., 3, 455 (1905).

in the earlier parts of this work and especially in the investigation, an account of which has recently appeared.[1]

The *freezing-point lowerings* produced by the various substances, over as wide range of dilution as was practicable, were measured. The more concentrated solutions were frozen by means of a mixture of solid carbon dioxide and alcohol, the freezing-temperatures being determined by means of alcohol thermometers. These temperatures could not be measured more closely than 0°.5, and we are not certain of our measurements for the very low temperatures to within 1°. For the more dilute solutions, Beckmann thermometers, covering a range of 5°, 12° and 25°, respectively, were used. When the more concentrated solutions were frozen they were removed from the bath of solid carbon dioxide and alcohol as soon as ice began to separate, in order that they might not be surrounded by the very cold freezing-mixture while temperature equilibrium was being established. The proper correction was introduced, in every instance, for the increase in concentration due to the separation of the ice. It was always a perfectly simple matter to ascertain when pure ice separated from the solution, or when some of the dissolved substance was deposited. This could usually be determined by the grit or sand-like character of the solid that separated, which was easily detected by rubbing the stirrer up and down in the freezing-tube. In all cases it could be detected by the behavior of the thermometer, as more and more of the solid was allowed to separate. When the cryohydric point was once reached the thermometer remained stationary as more and more of the solid separated. Otherwise, the thermometer would fall as more and more pure ice separated and increased the concentration of the solution. That solid solutions were formed seems highly improbable.

The *conductivities* of the solution were measured at 0°, in order to be able to ascertain, as nearly as possible, the dissociation at that temperature. The value of $\mu\infty$ was determined directly, whenever it was practicable to do so, simply by increasing the dilution of the solution until the molecular con-

[1] THIS JOURNAL, 33, 534 (1905).

ductivity reached a maximum, constant value. In other cases the value of $\mu\infty$ was obtained from the velocities of the ions in question and Kohlrausch's law ; $\mu\infty = a + c$.

It is well known that the conductivity method is not an accurate measure of dissociation in concentrated solutions. It is, however, an approximate method of measuring such dissociations and is the best we can do at present. All that can be said is, that it probably gives values of the right order of magnitude.

Since concentrated solutions contain, in a liter of solution, less than 1000 grams of water, it is necessary to determine the *specific gravities* of all such solutions, in order to correct the freezing-point lowering actually observed, for the difference between the amount of water really present in the solution and 1000 grams of water. The observed freezing-point lowering, thus corrected, can then be compared directly with the freezing-point constant of water, increased in terms of the percentage dissociation of the solution in question.

Calculation of the Approximate Composition of the Hydrates.

Given the above data, the calculation of the amount of water in combination with the dissolved substance is simple. The observed molecular lowering is corrected for the difference between 1000 grams and the amount of water actually present in 1 liter of the solution. This gives the true molecular lowering, produced by the substance at the dilution in question, if there were 1000 grams of water present.

The calculated molecular lowering can now be compared directly with the corrected, observed molecular lowering. If there was no hydration these two values would be equal. The magnitude of the hydration is obtained as follows :

The calculated molecular lowering is divided by the corrected molecular lowering found. This ratio, multiplied by 1000, gives the amount of water present playing the rôle of solvent, if the quantity of the substance present was dissolved in 1000 grams of water.

The difference between this amount of water and 1000 grams, is the quantity that is in combination with the dissolved sub-

stance, under the conditions that obtain in the solution in question.

For a number of reasons everything is referred to 1000 grams of the solvent. The theoretical freezing-point constant is calculated for 1000 grams of the solvent and, by calculating the depression found for the same amount of the solvent, the two sets of results are comparable. Further, by referring everything to a constant amount of the solvent, the various results can be compared directly with one another.

If we know the number of grams of water that have combined with the dissolved substance, the number of gram-molecules of water that have entered into combination is obtained by dividing the above value by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water in combination with 1 molecule of the dissolved substance, when the amount of substance present in a liter of the solution is dissolved in 1000 grams of water.

The Results.

In order to calculate the composition of the hydrates formed by any given substance, at different dilutions, it is necessary to have the following values:

The lowering of the freezing-point produced by the dissolved substance.

The conductivity of the solution as an approximate measure of its dissociation.

The specific gravities of the solutions, in order to calculate the difference between 1000 grams of water and the amount contained in a liter of the solution.

Some of the above data were already available for the following substances. However, in a few cases a part of the data had been secured and this we have supplemented wherever necessary.

The compositions of the hydrates, formed by the following substances, are calculated as closely as seems to be possible: Lithium iodide, sodium bromide, strontium nitrate, barium iodide, cadmium nitrate, chromium chloride, potassium ferrocyanide, potassium ferricyanide, sodium chromate, sodium di-

chromate, disodium phosphate, ammonium cupric chloride, potassium cupric chloride, ammonium sodium acid phosphate, hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, chromic acid, sodium hydroxide, potassium hydroxide and ammonium hydroxide.

In the various tables of data the symbols have the following significance:

In the tables of freezing-point measurements, m is the concentration, in terms of gram-molecules per liter; Δ the observed freezing-point lowering, corrected for the separation of ice and $\frac{\Delta}{m}$ the molecular lowering of the freezing-point.

In the conductivity tables the symbols have the usual significance, v is the volume of the solution, or the number of liters that contain a gram-molecular weight of the electrolyte; α is the approximate dissociation.

In the specific gravity tables m is the concentration; $W_{Sol.}$ the weight of 25 cc. of the solution; W_{Salt} the weight of the salt contained in 25 cc. of the solution; and W_{H_2O} the weight of water contained in 25 cc. of the solution. The percentage correction is the correction that must be applied to the freezing-point lowering, in order to refer it to 1000 grams of solvent, instead of the amount of water that is present in a liter of the solution in question.

The symbols in the hydrate tables have the following significance; m is the concentration in terms of gram-molecules per liter; α the approximate dissociation of the solution; L the theoretical molecular lowering of the freezing-point referred to 1000 grams of the solvent; $\frac{\Delta}{m}$ the molecular lowering found experimentally; L' the molecular lowering; m' the number of gram-molecules of water in combination, both being referred to 100 grams of water; H the number of molecules of water in combination with 1 molecule of the salt, at the concentration in question, if a liter of the solution, at that concentration, contained 1000 grams of water.

In order to ascertain the number of molecules of water actually in combination with 1 molecule of the dissolved sub-

stance, at the concentration given, it is only necessary to divide the value of m' for that concentration, by the concentration expressed in terms of a gram-molecular weight in 1000 grams of the solvent. The difference between the values of H found by these two methods is generally quite negligible, being smaller than experimental errors. It becomes appreciable only when the "correction" per cent is large, *i. e.*, in very concentrated solutions.

Lithium Iodide.

The freezing-point, conductivity and specific gravity measurements were made by Jones and Getman.[1] We find a somewhat higher value for $\mu\infty$, which makes the dissociations lower.

The total amount of water in combination with the salt increases with the concentration of the solution, in a fairly regular manner, as is shown in the curve, Fig. I. The number of

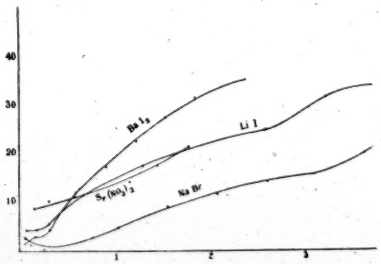


Fig. I.

molecules of water in combination with 1 molecule of the salt, increases from the most concentrated to the most dilute solution.

[1] Z. physik. Chem., 49, 391 (1904).

Table I.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.080	0°.296	3.70
0.161	0°.588	3.65
0.322	1°.218	3.79
0.645	2°.700	4.19
1.290	6°.140	4.75
2.580	16°.200	6.28
3.22	25°.000	7.76
5.16	59°.000	11.43

Table II.—Conductivity Measurements.

$\mu\infty$ 0° = 62.0.

v.	μ_v 0°.	α.
0.18	23.63	39.1
0.31	34.27	55.4
0.38	42.00	67.7
0.77	42.50	68.5
1.55	46.44	74.9
3.10	49.50	79.8
6.21	49.65	80.1
12.50	51.40	82.9

Table III.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.080	25.1427	0.2678	24.8749	0.50
0.161	25.3482	0.5389	24.8093	0.76
0.322	25.7813	1.0779	24.7034	1.19
0.645	26.6130	2.1341	24.4789	2.08
1.29	28.1726	4.3183	23.8533	4.59
2.58	31.2754	8.6365	22.5389	9.84
3.22	32.9292	10.7789	22.1503	11.40
5.16	37.5566	17.2731	20.2835	18.87

Table IV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$	L′.	m'.	H.
0.080	0.829	3.40	3.70	3.68	4.23	52.8
0.161	0.801	3.35	3.65	3.63	4.29	26.6
0.322	0.798	3.34	3.79	3.75	6.07	18.5
0.645	0.749	3.25	4.19	4.10	11.52	17.8
1.29	0.685	3.13	4.75	4.54	17.25	13.4
2.58	0.677	3.12	6.28	5.67	24.99	9.7
3.22	0.554	2.89	7.76	6.88	32.22	10.0
5.60	0.391	2.59	11.43	9.27	40.03	7.15

Sodium Bromide.

The freezing-point measurements, the conductivities and the specific gravities were worked out by Jones and Getman.[1]

We think the value 64.48 a little nearer the true value of $\mu\infty$ than the value 60.85, used by Jones and Getman. This alters somewhat the value of the dissociation and, consequently, the composition of the hydrates, as calculated.

The amount of water in combination is plotted against the concentration in the curve, Fig. I.

Table V.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.07	0°.245	3.77
0.13	0°.462	3.55
0.26	0°.907	3.49
0.52	1°.842	3.54
1.03	3°.815	3.70
1.55	6°.200	4.00
2.07	8°.610	4.16
2.59	11°.350	4.36
3.10	14°.000	4.52
3.62	18°.000	4.98

[1] Z. physik. Chem., 49, 394 (1904).

Table VI.—Conductivity Measurements.

$\mu\infty$ 0° = 64.48.

v.	μ_v 0°.	α.
0.27	34.52	53.5
0.32	37.78	58.6
0.38	40.26	62.4
0.48	43.39	67.3
0.64	46.07	71.4
0.97	48.31	74.9
1.92	51.12	79.3
3.85	54.00	83.7
7.69	55.38	85.8
15.38	59.02	91.5

Table VII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.07	25.1144	0.1802	24.9342	0.26
0.13	25.2390	0.3348	24.9042	0.38
0.26	25.4923	0.6695	24.8228	0.71
0.52	25.9538	1.3390	24.6128	1.54
1.03	27.0571	2.6780	24.3791	2.48
1.55	28.0156	3.9912	24.0244	3.90
2.07	29.0257	5.3302	23.6955	5.22
2.59	29.9884	6.6942	23.2942	6.82
3.10	30.9610	7.9825	22.9788	8.09
3.62	31.9614	9.3215	22.6399	9.44

Table VIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.07	0.915	3.56	3.77	3.76	2.96	42.2
0.13	0.858	3.46	3.55	3.54	1.26	9.66
0.26	0.837	3.42	3.49	3.47	0.43	1.65
0.52	0.793	3.32	3.54	3.49	2.70	5.20
1.03	0.749	3.25	3.70	3.61	5.54	5.38
1.55	0.714	3.19	4.00	3.84	9.40	6.07
2.07	0.673	3.11	4.16	3.94	11.70	5.65
2.59	0.624	3.02	4.36	4.06	14.23	5.49
3.10	0.586	2.95	4.52	4.15	16.06	5.18
3.62	0.535	2.86	4.98	4.51	20.33	5.62

Strontium Nitrate.

A solution of strontium nitrate was standardized and a new set of freezing-point measurements made. The total amount of water in combination, increases regularly with the concentration and the number of molecules of water, in combination with 1 molecule of the salt, increases from the most concentrated to the most dilute solution.

Table IX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.145	0°.68	4.70
0.290	1°.35	4.65
0.580	2°.44	4.20
1.161	4°.70	4.05
1.451	5°.85	4.03
1.741	7°.13	4.09
1.8137	7°.50	4.13

Table X.—Conductivity Measurements.

$\mu\infty$ 0° = 152.7.

v.	μ_v 0°.	α.
0.57	30.00	19.6
0.68	34.00	22.3
0.86	40.60	26.6
1.72	56.70	37.1
3.45	76.60	50.2
6.89	80.90	53.0
13.88	90.86	59.5

Table XI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction. Per cent.
0.145	25.6525	0.7676	24.8849	0.46
0.290	26.2575	1.5353	24.7222	1.11
0.580	27.5152	3.0705	24.4447	2.22
1.161	30.7750	6.1463	24.6287	1.48
1.451	32.5280	7.6816	24.8464	0.61
1.741	34.4900	9.2168	25.2732	—1.09
1.8137	35.0225	9.6017	25.4208	—1.68

Table XII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.145	0.530	3.93	4.70	4.68	8.91	61.4
0.290	0.502	3.73	4.65	4.60	10.51	36.2
0.580	0.371	3.24	4.20	4.11	11.73	20.2
1.161	0.266	2.95	4.05	3.99	14.48	12.5
1.451	0.223	2.69	4.03	4.01	18.29	12.6
1.741	0.196	2.59	4.09	4.13	20.72	11.3

Barium Iodide.

The freezing-points, conductivities and specific gravities are taken from the work of Jones and Getman.[1] The value 143 seems a little nearer to the true value of $\mu\infty$ at 0° than the value previously used. This changes, slightly, the values for the dissociation. While the total amount of combined water increases with the concentration (see curve, Fig. I.), the number of molecules of water combined with 1 molecule of the dissolved substance is nearly constant for all the dilutions studied.

Table XIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.076	0°.374	4.92
0.153	0°.764	5.00
0.306	1°.584	5.17
0.612	3°.720	6.08
0.917	6°.130	6.69
1.222	9°.220	7.54
1.528	13°.250	8.67
1.834	17°.500	9.54
2.139	24°.000	11.22

[1] Z. physik. Chem., 49, 408 (1904).

Table XIV.—Conductivity Measurements.

$\mu\infty$ 0°= 143.

v.	μ_v 0°.	*α.*
0.32	39.60	27.7
0.37	50.10	35.0
0.47	64.40	45.0
0.54	73.10	51.1
0.65	79.34	55.5
0.82	87.36	61.1
1.09	92.66	64.8
1.61	101.52	71.0
3.26	105.72	74.9
6.53	108.50	75.9
13.16	112.45	78.6

Table XV.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.076	25.6084	0.6843	24.9241	0.30
0.153	26.2575	1.4662	24.7913	0.83
0.306	27.4888	2.9325	24.5563	1.77
0.612	30.0284	5.9628	24.0656	3.74
0.917	32.5060	8.9930	23.513	5.95
1.222	35.0114	11.9255	23.0859	7.46
1.528	37.5227	14.9557	22.5670	9.73
1.834	40.0067	17.8882	22.1185	11.53
2.139	42.4761	20.9185	21.5576	13.77

Table XVI.—Hydrates.

m.	*α.*	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.076	0.786	4.78	4.92	4.91	1.47	19.3
0.153	0.759	4.68	5.00	4.96	3.14	20.5
0.306	0.749	4.65	5.17	5.08	4.70	15.4
0.612	0.710	4.54	6.08	5.86	12.51	20.4
0.917	0.648	4.27	6.69	6.29	17.84	19.5
1.222	0.611	4.13	7.54	6.98	22.70	18.1
1.528	0.555	3.92	8.67	7.83	27.74	18.2
1.834	0.511	3.76	9.54	8.44	31.92	17.4
2.139	0.450	3.53	11.22	9.67	35.28	16.5

Cadmium Nitrate.

According to the earlier work, cadmium nitrate gave somewhat too great lowering of the freezing-point, for a salt with 4 molecules of water of crystallization. Having repeated the work with this substance, we find somewhat smaller lowerings, the difference probably being due to some error in the original work, possibly in the standardization of the solution. We find that the salt gives just about the lowering that we should expect from its water of crystallization.

The results for the amount of combined water are plotted in Fig. II. The number of molecules of water combined with 1

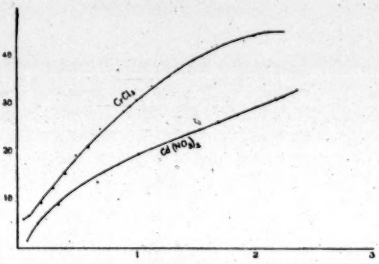


Fig. II.

molecule of the dissolved substance increases with the dilution of the solution.

Table XVII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0845	0°.41	4.85
0.1691	0°.85	5.03
0.3382	1°.73	5.12
0.6764	3°.50	5.18
1.0146	5°.73	5.65
1.6910	10°.58	6.38
2.3674	17°.00	7.18

Table XVIII.—Conductivity Measurements.

$\mu\infty$ 0° = 116.5.

v.	μ_v 0°.	*α.*
0.42	23.47	20.1
0.59	34.27	29.4
0.98	50.22	43.1
1.48	59.00	50.7
2.95	73.42	63.0
5.91	83.55	71.7
11.83	87.17	74.8

Table XIX.—Specific Gravity Determinations.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0845	25.3835	0.4995	24.8840	0.46
0.1691	25.8521	0.9990	24.8531	0.59
0.3382	26.6653	1.9980	24.6673	1.33
0.6764	28.1045	3.9960	24.1085	3.57
1.0146	29.7375	5.9940	23.7435	5.03
1.6910	32.7386	9.9900	22.7486	9.01
2.3674	35.5865	13.9860	21.6005	13.60

Table XX.—Hydrates.

m.	*α.*	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.0845	0.748	4.64	4.82	4.80	1.85	21.9
0.1691	0.717	4.53	5.03	5.00	5.22	30.9
0.3382	0.630	4.20	5.12	5.05	9.36	27.7
0.6764	0.507	3.75	5.18	5.00	13.89	20.5
1.0146	0.431	3.46	5.65	5.37	19.76	19.5
1.6910	0.294	2.94	6.38	5.81	26.49	15.7
2.3674	0.201	2.51	7.18	6.20	33.06	13.9

Chromium Chloride.

The chloride of chromium is an interesting substance to study in the present connection, on account of it being a quarternary electrolyte, having 6 molecules of water of crystallization and being very soluble in water.

The results are just what would have been expected from our earlier work with similar compounds. The total amount of water combined with the salt is large and increases from the most dilute to the most concentrated solution (see Fig. II.).

The number of molecules of water combined with 1 molecule of the dissolved substance is, as would be expected, large, and increases from the most concentrated to the most dilute solution.

Table XXI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.268	5.36
0.1	0°.510	5.10
0.2	1°.030	5.15
0.3	1°.570	5.23
0.4	2°.160	5.45
0.5	2°.910	5.82
0.6	3°.610	6.016
0.7	4°.55	6.50
0.9	6°.30	7.00
1.0	7°.46	7.46
1.5	15°.00	10.00
2.0	27°.00	13.50
2.25	33°.00	14.67

Table XXII.—Conductivity Measurements.

$\mu\infty$ 0° = 190.

v.	μ_v 0°.	α.
0.40	14.46	7.61
0.44	18.31	9.64
0.50	22.60	11.63
0.67	32.19	16.94
1.00	45.40	23.90
1.11	48.62	25.60
1.43	55.47	29.20
1.67	59.27	31.20
2.00	63.12	33.22
2.50	68.11	35.85
3.33	72.37	38.10
5.00	79.70	41.95
10.00	89.14	46.92
20.00	100.2	52.73

Table XXIII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.2479	0.1981	25.0498	0.20
0.1	25.3552	0.3961	24.9591	0.16
0.2	25.6458	0.7923	24.8535	0.59
0.3	25.9221	1.1884	24.7337	1.06
0.4	26.2676	1.5845	24.6831	1.27
0.5	26.5693	1.9806	24.5887	1.64
0.6	26.9335	2.3768	24.5567	1.77
0.7	27.2232	2.7729	24.4503	2.20
0.9	27.7939	3.5651	24.2288	3.09
1.0	28.0684	3.9613	24.1071	3.57
1.5	29.5153	5.9419	23.5734	5.71
2.0	30.9932	7.9225	23.0207	7.92
2.25	31.5784	8.9128	22.6656	9.34

Table XXIV.—Hydrates.

m.	*a.*	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.05	0.527	4.80	5.36	5.37	5.90	117.94
0.1	0.469	4.48	5.10	5.09	6.66	66.58
0.2	0.420	4.20	5.15	5.12	9.98	49.91
0.3	0.381	3.99	5.23	5.18	12.76	42.54
0.4	0.359	3.86	5.45	5.38	15.70	39.24
0.5	0.332	3.71	5.82	5.73	19.58	39.17
0.6	0.312	3.60	6.01	5.91	21.16	35.27
0.7	0.292	3.49	6.50	6.36	25.07	35.81
0.9	0.256	3.29	7.00	6.78	28.60	31.78
1.0	0.239	3.19	7.46	7.19	30.91	30.91
1.5	0.169	2.80	10.00	9.43	39.05	26.04
2.0	0.116	2.52	13.50	12.42	44.28	22.14
2.25	0.096	2.40	14.67	13.30	45.53	20.24

Potassium Ferrocyanide.

This salt was chosen, on account of the statement in the literature that it dissociates thus, $\overset{+}{K},\overset{+}{K},\overset{+}{K},\overset{+}{K},(\overline{\overline{Fe(CN)_6}}$, yielding 5 ions. We shall see, later, that this is doubtful. The molecular lowerings of the freezing-point that were produced

were small; indeed, so small that there was no evidence of any appreciable hydration in the solutions. We then took up the problem as to whether there is *any appreciable time factor in the conductivity* of solutions of potassium ferrocyanide. The following solutions of the salt were prepared and their conductivities determined at 25°.

v.	μ_v 25°.
40	369.4
80	405.5
160	447.8
320	496.2
400	507.4

After making these measurements the solutions were allowed to remain in the thermostat-bath, for 30 minutes and their conductivities redetermined. No appreciable change was detected. The conductivities were measured again, after the solutions had stood for 4 hours and still no change of any moment manifested itself. The same result was obtained after the solutions had stood for more than 24 hours.

A change in the conductivity might have occurred before the first conductivity measurements were made. To test this, some of the salt was weighed in the dry conductivity cup and a known quantity of water, which had already been brought to the temperature of the bath, added. In a very few minutes the first conductivity reading was made. The conductivity did not change an appreciable amount on allowing the solutions to stand.

It was then decided to determine whether there is any *change in the freezing-point lowering with time.* Fresh solutions were prepared and their freezing-points determined immediately. The solutions were then allowed to stand and their freezing-points determined from time to time. No change could be detected.

The *value of* $\mu\infty$ was then determined for potassium ferrocyanide, at 25°, with the following result:

v.	μ_v 25°.
640	530
1280	557
2560	580
5120	575

The value of $\mu\infty$ seems to have been reached at a dilution of from 3000–5000 liters.

Dissociation of Potassium Ferrocyanide.

The magnitude of this value throws some light on the question as to how potassium ferrocyanide dissociates. It is almost exactly the value that would have been obtained if potassium ferrocyanide dissociated thus :

$$K_4Fe(CN)_6 = \overset{+}{K},\overset{+}{K},\overset{+}{K},\overset{-}{CN},\overset{-}{CN},\overset{-}{CN},\overset{+}{K},Fe\overset{-}{(CN)_3}.$$

Table XXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.580	5.80
0.2	1°.05	5.25
0.3	1°.45	4.83
0.4	1°.78	4.45

Table XXVI.—Conductivity Measurements.

v.	μ_v 0°.
2.00	154.1
2.50	156.0
3.33	158.4
5.00	163.4
10.00	171.8

Table XXVII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.1	25.6794	0.9221	24.7573	0.97
0.2	26.2775	1.8442	24.4333	2.27
0.3	26.8744	2.7663	24.1081	3.57
0.4	27.5021	3.6884	23.8137	4.75
0.5	28.0540	4.6105	23.4435	6.23

Potassium Ferricyanide.

The freezing-point lowerings were small and, therefore, the salt showed no hydration.

Dissociation of Potassium Ferricyanide.

Light could be thrown on the *way in which potassium ferricyanide dissociated*, by comparing the conductivity of this salt with that of potassium ferrocyanide at the same dilutions. The differences were just about what would be expected, if the solutions of the ferrocyanide contained one more molecule of potassium cyanide than those of the ferricyanide. From this we conclude that potassium ferricyanide dissociates thus:

$$K_3Fe(CN)_6 = \overset{+}{K},\overset{-}{CN},\overset{+}{K},\overset{-}{CN},\overset{+}{K},\overset{-}{Fe(CN)_4}.$$

This is also in accord with the value found for $\mu\infty$ for this substance.

Table XXVIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.30	6.00
0.1	0°.56	5.60
0.2	1°.086	5.43
0.3	1°.57	5.23
0.4	2°.05	5.12

Table XXIX.—Conductivity Measurements.

v.	μ_v 0°.
2.50	146.1
3.33	149.2
5.00	154.3
10.00	162.8
20.00	172.4

Table XXX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.2408	0.4121	24.8287	0.69
0.1	25.5037	0.8242	24.6795	1.28
0.2	25.9084	1.6483	24.2601	2.96
0.3	26.3277	2.4725	23.8552	4.58
0.4	26.8154	3.2966	23.5188	5.93

Sodium Chromate.

Sodium chromate, being fairly soluble, was brought within the scope of this work. It was not expected that the chromates would give normal results, but, like the sulphates, would behave abnormally. It is quite possible that the chromate is somewhat polymerized and that this is offset by the hydration. The results would indicate the power to combine with a small amount of water in the more concentrated solutions.

Solutions of greater concentrations could not be used, on account of the salt separating out at the low temperatures.

Table XXXI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.450	4.50
0.2	0°.850	4.25
0.3	1°.230	4.10
0.4	1°.604	4.01
0.5	1°.960	3.92
0.6	2°.345	3.90
0.8	3°.063	3.83
1.0	3°.800	3.80

Table XXXII.—Conductivity Measurements.

v.	μ_v 0°.	α.
1.00	53.95	45.0
1.25	57.59	48.0
2.00	69.0	57.5
2.50	72.5	60.4
3.33	76.0	63.5
5.00	80.0	66.7
10.00	89.4	74.5
20.00	97.0	80.8

Table XXXIII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.1875	0.2028	24.9847	0.06
0.10	25.3800	0.4055	24.9745	0.10
0.20	25.7175	0.8110	24.9065	0.37
0.30	26.0600	1.2165	24.8435	0.62
0.40	26.4025	1.6220	24.7805	0.88
0.50	26.7325	2.0275	24.7050	1.18
0.60	27.0850	2.4330	24.6520	1.39
0.80	27.7500	3.2440	24.5060	1.98
1.00	28.4150	4.0550	24.3600	2.56

Table XXXIV.—Hydrates.

m.	*a.*	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.05	0.808	4.86	4.86	4.86	..	..
0.10	0.745	4.63	4.50	4.50	..	..
0.20	0.667	4.34	4.25	4.23	..	..
0.30	0.635	4.22	4.10	4.07	..	..
0.40	0.604	4.11	4.01	3.97	..	..
0.50	0.575	4.00	3.92	3.87	..	..
0.60	0.543	3.88	3.91	3.86	..	..
0.80	0.480	3.64	3.83	3.75	1.67	2.1
1.00	0.450	3.53	3.80	3.70	2.55	2.55

Sodium Dichromate.

Sodium dichromate was quite readily soluble in water at ordinary temperatures, but, at the freezing-points the solubility was greatly diminished. We could, therefore, work only with fairly dilute solutions.

The results show very considerable hydrating power on the part of sodium dichromate, which increases with fair regularity from the most concentrated to the most dilute solution.

The results for the dichromate cannot, of course, be compared with those for the chromate, as the two compounds are

salts of such different acids. The dichromate behaves about as would be expected.

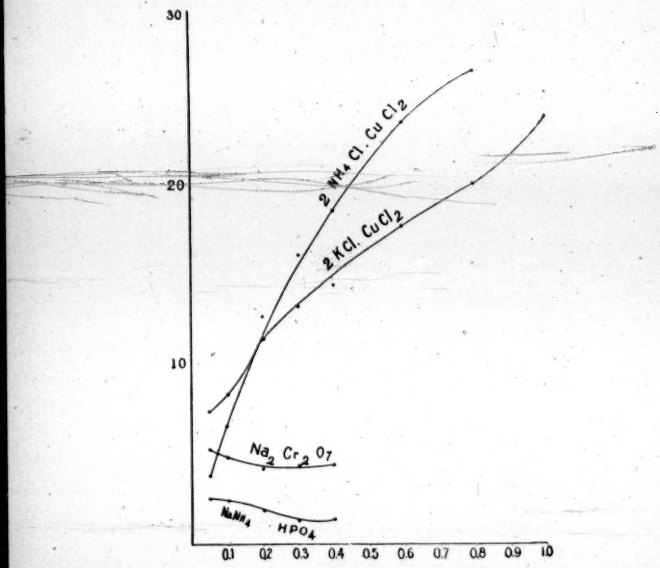


Fig. III.

Table XXXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.490	4.90
0.2	0°.946	4.73
0.3	1°.400	4.66
0.4	1°.872	4.68

Table XXXVI.—Conductivity Measurements.

$\mu\infty$ 0° = 125.5.

v.	μ_v 0°.	α.
2.50	81.5	65.0
3.33	85.7	68.2
5.00	89.0	71.0
10.00	95.0	75.7
20.00	100.8	80.5

Table XXXVII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.2375	0.3304	24.9071	0.37
0.10	25.4750	0.6607	24.8143	0.74
0.20	25.9425	1.3215	24.6210	1.52
0.30	26.4200	1.9822	24.4378	2.25
0.40	26.8900	2.6430	24.2470	3.01
0.60	27.8050	3.9644	23.8406	4.64
0.80	28.7275	5.2860	23.4415	6.23
1.00	29.6225	6.6075	23.0150	7.94
1.25	30.7125	8.2594	22.4531	10.19

Table XXXVIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.10	0.757	4.68	4.90	4.86	2.05	20.5
0.20	0.710	4.50	4.73	4.66	1.94	9.7
0.30	0.682	4.40	4.66	4.56	1.94	6.5
0.40	0.650	4.28	4.68	4.54	3.16	7.9

Disodium Phosphate.

Disodium phosphate was an especially interesting salt to study, in the present connection, on account of the large amount of water with which it crystallizes. It crystallizes with more water (12 molecules) than any other salt thus far employed in the present connection. It is unfortunate that the salt has such slight solubility in water at the freezing-point of the solutions. We were not able to study solutions more concentrated than 0.1 N.

The results, however, show conclusively that disodium phosphate has greater power to combine with water than any other substance that we have investigated, which is of importance in connection with our relation between water of crystallization and lowering of freezing-point.

Table XXXIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.427	4.27
0.05	0°.237	4.74

Table XL.—Conductivity Measurements.

v.	μ_v 0°.	α.
10	62.8	34.9
20	70.6	39.2

Table XLI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.1	25.4325	0.3553	25.0772	—0.31
0.5	25.2580	0.1776	25.0806	0.32

Table XLII.—Hydrates.

m.	α.	L_v.	$\frac{\Delta}{m}$.	L'.	m'.	H.
0.05	0.392	3.32	4.74	4.75	16.72	334.4
0.10	0.349	3.22	4.27	4.28	13.76	137.6

Ammonium Sodium Acid Phosphate.

The ammonium sodium acid phosphate crystallizes with 4 molecules of water and was, therefore, of interest from our standpoint. It combines with considerable water, especially in the dilute solutions, indeed, with just about the amount that we should expect from its water of crystallization.

The phosphates, then, fall in line with the general relation between water of crystallization and lowering of freezing-point.

Table XLIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.224	4.45
0.1	0°.420	4.20
0.2	0°.773	3.87
0.3	1°.088	3.63
0.4	1°.408	3.52

Table XLIV.—Conductivity Measurements.

$\mu\infty$ 0° = 120.

v.	μ_v 0°.	α.
2.5	49.1	0.409
3.33	53.1	0.443
5.0	59.5	0.500
10.0	69.0	0.575
20.0	76.7	0.639

Table XLV.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.1425	0.1714	24.9711	0.12
0.1	25.2775	0.3428	24.9347	0.26
0.2	25.5500	0.6857	24.8643	0.54
0.3	25.7925	1.0285	24.7640	0.94
0.4	26.0575	1.3714	24.6861	1.26

Table XLVI.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.639	4.24	4.45	4.45	2.61	52.2
0.10	0.575	4.00	4.20	4.19	2.50	25.0
0.20	0.500	3.72	3.87	3.85	1.88	9.4
0.30	0.443	3.51	3.63	3.60	1.39	4.6
0.40	0.409	3.38	3.52	3.48	1.55	3.9

Ammonium Cupric Chloride.

Having studied a large number of the salts of simple acids, we extended our work so as to include a few salts of complex

acids. We selected the double chloride of ammonium and copper, since it could readily be obtained in a pure condition.

When the double chlorides dissolve in water they break down, for the most part, into the single salts, as has been shown by Jones and Knight.[1] The power to combine with water would, then, be essentially the power of the single salts to combine with it in the presence of one another.

Table XLVII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.600	12.00
0.1	1°.214	12.14
0.2	2°.515	12.57
0.3	3°.964	13.21
0.4	5°.500	13.75
0.6	8°.700	14.50
0.8	12°.00	15.00
1.0		

Table XLVIII.—Conductivity Measurements.

v.	μ_v 0°.	α.
1.00	130.4	43.6
1.25	146.1	48.9
1.66	162.9	54.5
2.50	187.4	62.7
3.33	197.6	66.1
5.00	205.6	68.7
10.00	235.1	78.5
20.00	248.6	83.2

Table XLIX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction. Per cent.
0.05	25.1975	0.2919	24.9056	0.38
0.1	25.3875	0.5837	24.8038	0.78
0.2	25.7925	1.1674	24.6251	1.50
0.3	26.2075	1.7511	24.4564	2.17
0.4	26.5875	2.3348	24.2527	2.99
0.6	27.3200	3.5022	23.8178	4.73
0.8	28.0675	4.6696	23.3979	6.41

[1] THIS JOURNAL, 33, 110 (1899).

Table L.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.832	11.14	12.00	11.96	3.83	76.6
0.10	0.785	10.62	12.14	12.05	6.61	66.1
0.20	0.687	9.54	12.57	12.39	12.77	63.85
0.30	0.661	9.23	13.31	13.02	16.18	53.9
0.40	0.627	8.86	13.75	13.34	18.66	46.65
0.60	0.545	7.94	14.50	13.82	23.64	39.4
0.80	0.489	7.32	15.00?	14.04	26.59	33.23
1.00	0.436					

Potassium Cupric Chloride.

Another salt of a complex acid, which we could readily obtain in pure condition, was potassium cupric chloride. This, like the corresponding ammonium salt, breaks down in solution, into the two single chlorides. The total amount of water in combination increases very regularly from the most dilute to the most concentrated solution, and the number of molecules of water in combination with one of the salt, or the resulting ions, increases from the most concentrated to the most dilute solution.

Table LI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.623	12.46
0.1	1°.200	12.00
0.2	2°.425	12.12
0.3	3°.668	12.23
0.4	5°.00	12.50
0.6	7°.50	12.50
0.8	10°.00	12.50
1.0	13°.00	13.00

Table LII.—Conductivity Measurements.

v.	μ_v 0°.	α.
1.00	127.0	44.3
1.25	143.3	50.0
1.66	159.0	55.5
2.50	183.6	64.1
3.33	186.0	65.0
5.00	196.5	68.5
10.00	212.0	74.0
20.00	228.1	79.6

Table LIII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.2625	0.3546	24.9079	0.37
0.1	25.5225	0.7092	24.8133	0.75
0.2	26.0600	1.4184	24.6416	1.43
0.3	26.5825	2.1276	24.4549	2.18
0.4	27.1075	2.8368	24.2707	2.92
0.6	28.1175	4.2552	23.8613	4.55
0.8	29.1100	5.6736	23.4364	6.25
1.0	30.0875	7.0920	22.9955	8.02

Table LIV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.796	10.74	12.46	12.41	7.48	149.6
0.1	0.740	10.11	12.00	11.91	8.40	84.0
0.2	0.685	9.50	12.12	11.95	11.39	56.9
0.3	0.650	9.11	12.23	11.97	13.28	44.3
0.4	0.641	9.02	12.50	12.14	14.28	35.7
0.6	0.555	8.05	12.50	11.93	18.07	30.1
0.8	0.500	7.44	12.50	11.72	20.29	25.4
1.0	0.443	6.80	13.00	11.96	23.97	24.0

Hydrochloric Acid.

Having investigated a fairly large number of salts we then studied some of the more common acids and measured the freezing-point lowerings produced by solutions as concentrated as could be used with the thermometers at our disposal. Dilutions ranging from 6 N to 0.05 N were employed.

In very dilute solutions hydrochloric acid does not seem to have the power of combining with water. The amount of combined water increases with the concentration, from about 0.3 N to the most concentrated solution that was studied (see curve, Fig. IV.).

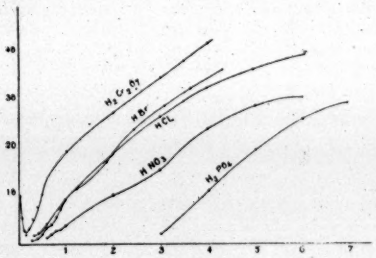


Fig. IV.

A possible explanation of the fact that, in dilute solutions, hydrochloric acid does not combine with water at all, is given at the end of this paper, under the general discussion.

Table LV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.174	3.59
0.1	0.355	3.55
0.2	0.712	3.56
0.3	1.080	3.60
0.4	1.442	3.60
0.5	1.832	3.66
0.6	2.250	3.75
0.7	2.634	3.76
0.8	3.070	3.84
0.9	3.540	3.93
1.0	4.100	4.10
2.0	9.937	4.97
3.0	18.100	6.03
4.0	30.5	7.62
5.0	44.0	8.80
6.0	61.0	10.16

Table LVI.—Conductivity Measurements.

$\mu\infty$ 0° = 240.5.

v.	μ_v 0°.	α.
0.166	83.05	34.5
0.20	100.2	41.7
0.25	120.2	50.0
0.33	141.1	58.7
0.50	166.6	69.3
1.00	191.0	79.4
1.11	196.0	81.5
1.25	200.5	83.4
1.43	204.0	84.8
1.66	208.0	86.5
2.00	209.5	87.1
2.50	214.0	89.0
3.33	217.0	90.2
5.00	218.0	90.6
10.00	228.5	95.0
20.00	234.0	97.3

Table LVII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0017	0.0456	24.9551	0.18
0.1	25.0250	0.0911	24.9339	0.26
0.2	25.0716	0.1823	24.8893	0.44
0.3	25.1148	0.2734	24.8414	0.63
0.4	25.1289	0.3646	24.7643	0.94
0.5	25.1712	0.4557	24.7155	1.14
0.6	25.1949	0.5469	24.6480	1.41
0.7	25.2428	0.6380	24.6048	1.58
0.8	25.3075	0.7292	24.5783	1.69
0.9	25.3659	0.8203	24.5456	1.82
1.0	25.4510	0.9115	24.5395	1.84
2.0	25.7906	1.8230	23.9676	4.13
3.0	26.1606	2.7345	23.4261	6.30
4.0	26.5373	3.6460	22.8913	8.43
5.0	26.8555	4.5575	22.2980	10.81
6.0	27.2191	5.4690	21.7501	13.00

Table LVIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.972	3.67	3.59	3.58	—	—
0.1	0.950	3.63	3.55	3.54	—	—
0.2	0.906	3.55	3.56	3.54	—	—
0.3	0.902	3.54	3.60	3.58	0.62	2.07
0.4	0.890	3.51	3.60	3.57	0.89	2.24
0.5	0.871	3.48	3.66	3.62	2.13	4.26
0.6	0.865	3.47	3.75	3.70	3.44	5.74
0.7	0.848	3.44	3.76	3.70	3.90	5.58
0.8	0.834	3.41	3.84	3.78	5.44	6.80
0.9	0.815	3.37	3.93	3.86	7.05	7.83
1.0	0.794	3.34	4.10	4.02	9.40	9.40
2.0	0.693	3.15	4.98	4.77	18.86	9.43
3.0	0.586	2.95	6.03	5.65	26.55	8.85
4.0	0.500	2.79	7.62	6.98	33.35	8.34
5.0	0.417	2.64	8.80	7.85	36.87	7.37
6.0	0.345	2.49	10.16	8.84	39.91	6.65

Hydrobromic Acid.

The hydrobromic acid was kindly prepared for us by Professor Renouf. A fairly wide range of concentration was investigated. The results were very similar in character to those obtained with hydrochloric acid. The solutions up to about 0.3 N show no hydration. The hydration from this point to the most concentrated solution investigated, is of the same order as for hydrochloric acid (see Fig. III.).

The number of molecules of water in combination with 1 molecule of the acid is of the same magnitude with hydrobromic as with hydrochloric acid. It increases from about 0.3 N to 2 N and then decreases up to the most concentrated solution used. The meaning of this rather surprising fact will be pointed out in the general discussion of the results.

Table LIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1229	0°.451	3.67
0.1843	0°.657	3.56
0.2467	0°.880	3.57
0.3686	1°.350	3.69
0.4914	1°.845	3.75
0.614	2°.316	3.77
1.229	5°.440	4.42
1.843	9°.200	4.99
2.457	15°.0	6.10
3.072	21°.5	7.00
3.686	29°.0	7.87
4.30	41°.0	9.54

Table LX.—Conductivity Measurements.

$\mu\infty$ 0° = 246.

v.	μ_v 0°.	α.
0.23	115.8	47.1
0.27	129.3	52.6
0.33	145.8	59.3
0.41	171.0	69.5
0.54	174.7	71.0
0.82	194.2	78.9
1.63	211.7	86.1
2.03	220.3	89.6
2.71	224.0	91.1
4.07	227.5	92.5
5.43	230.5	93.7
8.14	238.2	96.8
16.28	244.0	99.2

Table LXI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.0614	25.0575	0.1243	24.9332	0.27
0.1229	25.1350	0.2487	24.8863	0.46
0.1843	25.2025	0.3730	24.8295	0.68
0.2457	25.2800	0.4973	24.7827	0.87
0.3686	25.4050	0.7460	24.6590	1.36
0.4914	25.5450	0.9946	24.5504	1.80
0.6143	25.7025	1.2433	24.4592	2.16
1.229	26.3925	2.4875	23.9050	4.38
1.843	27.0825	3.7302	23.3523	6.59
2.457	27.7850	4.9730	22.8120	8.75
3.072	28.4500	6.2177	22.2323	11.07
3.686	29.1525	7.4605	21.6920	13.23
4.300	29.8275	8.7032	21.1243	15.50
5.7297	31.4600	11.5075	19.9525	20.19

Table LXII.—Hydrates.

m.	*α*.	L.	$\frac{\Delta}{m}$.	L′.	*m*′.	H.
0.0614	0.992	3.71	..	..	—	—
0.1229	0.968	3.66	3.67	3.65	—	—
0.1843	0.937	3.60	3.56	3.54	—	—
0.2457	0.925	3.58	3.57	3.54	—	—
0.3686	0.911	3.55	3.69	3.64	1.67	4.53
0.4914	0.896	3.53	3.75	3.68	2.22	4.52
0.6143	0.861	3.46	3.77	3.69	3.50	5.70
1.229	0.789	3.33	4.42	4.23	11.82	9.62
1.843	0.710	3.18	4.99	4.66	17.65	9.58
2.457	0.695	3.15	6.10	5.57	24.10	9.80
3.072	0.593	2.96	7.00	6.23	29.17	9.48
3.686	0.526	2.84	7.87	6.83	32.40	8.79
4.300	0.471	2.74	9.54	8.06	36.65	8.52

Nitric Acid.

The results with nitric acid are of the same general character as those with hydrochloric and hydrobromic acids. The freezing-point lowerings are, however, less in the case of nitric acid and, since the dissociation is about the same, the hydrating power is smaller.

Like hydrochloric and hydrobromic acids, dilute solutions of nitric acid seem to form no hydrates. Not until about 0.7 N is reached, is there manifested any appreciable power to combine with water. The total amount of water combined with the acid increases with the concentration up to the most concentrated solution.

The number of molecules of water in combination with 1 molecule of the acid increases from about 0.7 N, with the concentration, to about 4 N and then begins to decrease with further increase in the concentration.

Table LXIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.175	3.51
0.10	0°.350	3.50
0.20	0°.696	3.48
0.30	1°.05	3.50
0.40	1°.415	3.54
0.50	1°.79	3.58
0.60	2°.20	3.66
0.70	2°.59	3.70
0.80	3°.00	3.75
0.90	3°.39	3.77
1.00	3°.806	3.806
2.00	8°.410	4.205
3.00	13°.908	4.636
4.00	23°.00	5.75
5.00	32°.50	6.50
6.00	42°.00	7.00

Table LXIV.—Conductivity Measurements.

$\mu\infty$ 0° = 235.6.

v.	μ_v 0°.	α.
0.166	89.4	37.9
0.20	108.0	45.8
0.25	127.1	53.9
0.33	148.9	63.2
0.50	174.0	73.9
1.00	199.5	84.8
1.11	204.0	86.7
1.25	205.5	87.3
1.43	207.0	88.0
1.66	209.2	88.9
2.00	215.0	91.2
2.50	218.6	92.8
3.33	222.1	94.3
5.00	226.1	96.0
10.00	228.5	97.0
20.00	232.5	98.7

Table LXV.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0150	0.0788	24.9362	0.26
0.1	25.0575	0.1576	24.8999	0.40
0.2	25.1425	0.3153	24.8272	0.69
0.3	25.2250	0.4729	24.7521	0.99
0.4	25.3050	0.6305	24.6745	1.30
0.5	25.3900	0.7881	24.6019	1.55
0.6	25.4750	0.9458	24.5292	1.88
0.7	25.5825	1.1034	24.4791	2.08
0.8	25.6400	1.2610	24.3790	2.48
0.9	25.6953	1.4186	24.2767	2.89
1.0	25.7700	1.5763	24.1937	3.23
2.0	25.6193	3.1525	23.4668	6.13
3.0	27.4660	4.7287	22.7373	9.05
4.0	28.2364	6.3050	21.9314	12.25
5.0	29.0029	7.8813	21.1216	15.51
6.0	29.7758	9.4575	20.3183	18.73

Table LXVI.—Hydrates.

m.	*α.*	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.05	0.987	3.70	3.51	3.50	—	—
0.1	0.970	3.66	3.50	3.49	—	—
0.2	0.960	3.65	3.48	3.46	—	—
0.3	0.943	3.61	3.50	3.47	—	—
0.4	0.928	3.59	3.54	3.49	—	—
0.5	0.912	3.56	3.58	3.52	—	—
0.6	0.889	3.51	3.66	3.59	1.24	2.07
0.7	0.880	3.50	3.70	3.62	1.84	2.63
0.8	0.873	3.48	3.75	3.66	2.73	3.41
0.9	0.867	3.47	3.77	3.66	2.88	3.20
1.0	0.848	3.44	3.81	3.69	3.76	3.76
2.0	0.739	3.23	4.21	3.95	10.13	5.06
3.0	0.632	3.04	4.64	4.22	15.53	5.18
4.0	0.539	2.86	5.75	5.05	24.09	6.02
5.0	0.458	2.61	6.50	5.49	29.14	5.83
6.0	0.379	2.56	7.00	5.69	30.56	5.09

Phosphoric Acid.

The freezing-point lowerings produced by phosphoric acid are so small that, although the dissociation is not large, the amount of hydration is small, manifesting itself only in the more concentrated solutions.

Table LXVII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.235	2.35
0.2	0°.458	2.29
0.3	0°.667	2.22
0.4	0°.868	2.17
0.6	1°.292	2.15
0.8	1°.775	2.22
1.0	2°.370	2.37
2.0	5°.550	2.77
3.0	9°.75	3.25
4.0	16°.50	4.12
5.0	25°.00	5.00
6.0	38°.00	6.33
6.919	52°.00	7.52

Table LXVIII.—Conductivity Measurements.

$\mu\infty$ 0° = 240.

v.	μ_v 0°.	*α.*
0.14	20.00	8.3
0.16	23.4	9.8
0.20	26.8	11.2
0.25	31.6	14.3
0.33	35.2	14.7
0.50	38.0	16.1
1.00	42.0	17.5
1.11	42.6	17.8
1.25	43.0	17.9
1.43	44.4	18.3
1.66	45.1	18.8
2.00	45.8	19.1
2.50	47.5	19.8
3.33	50.0	20.8
5.00	61.5	25.6
10.00	68.6	28.6
20.00	85.5	35.6

Table LXIX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0550	0.1225	24.9325	0.27
0.10	25.1025	0.2450	24.8575	0.57
0.20	25.2425	0.4900	24.7525	0.99
0.30	25.3750	0.7350	24.6400	1.44
0.40	25.5075	0.9800	24.5275	1.89
0.50	25.6375	1.2250	24.4125	2.35
0.60	25.7650	1.4700	24.2950	2.82
0.6916	25.9100	1.6952	24.2148	3.14
0.80	26.0200	1.9600	24.0600	3.76
0.90	26.1575	2.2050	23.9525	4.29
1.00	26.2900	2.4500	23.8400	4.64
2.00	27.6175	4.9000	22.7175	9.13
3.00	28.8875	7.3500	21.5375	13.85
4.00	31.1775	9.8000	21.2775	18.89
5.00	31.4975	12.2500	19.2475	23.01
6.00	32.7050	14.7000	18.0050	27.98
6.919	33.5725	16.9516	16.6209	33.52

Table LXX.—Hydrates.

m.	a.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.1	0.286	3.46	2.35	2.34	—	—
0.2	0.256	3.29	2.29	2.27	—	—
0.3	0.208	3.02	2.22	2.19	—	—
0.4	0.198	2.96	2.17	2.13	—	—
0.6	0.188	2.91	2.15	2.09	—	—
0.8	0.179	2.86	2.22	2.14	—	—
1.0	0.175	2.84	2.37	2.26	—	—
2.0	0.161	2.76	2.77	2.52	—	—
3.0	0.147	2.68	3.25	2.80	2.38	0.79
4.0	0.143	2.66	4.12	3.33	11.18	2.79
5.0	0.112	2.48	5.00	3.85	19.77	3.95
6.0	0.098	2.41	6.33	4.56	26.19	4.37
6.919	0.083	2.32	7.52	5.00	29.78	4.34

Chromic Acid.

Chromic acid gives large freezing-point lowerings at all of the dilutions studied and, not being very highly dissociated, it therefore has great power to form hydrates. As Ostwald pointed out, chromic acid exists in solution, in the form of dichromic acid, the hydrogen ions effecting the transformation. The amount of combined water increases regularly with the concentration (see Fig. IV.) and the amount of water in combination with 1 molecule of the acid increases, in general, with the dilution of the solution.

Table LXXI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.10	0°.526	5.26
0.15	0°.775	5.16
0.20	1°.050	5.24
0.30	1°.610	5.36
0.40	2°.22	5.54
0.50	2°.89	5.78
1.00	6°.78	6.78
1.50	11°.47	7.64
2.00	16°.00	8.00
2.50	22°.5	9.00
3.00	31°.0	10.40
3.50	42°.0	12.00
4.00	57°.5	14.40

Table LXXII.—Conductivity Measurements.

$\mu\infty$ 0° = 523.

v.	μ_v 0°.	α.
0.286	108.4	20.7
0.333	128.2	24.5
0.400	157.3	30.0
0.500	206.8	39.3
0.666	256.2	49.0
1.000	312.4	59.7
2.000	374.3	71.6
2.500	388.9	74.3
3.33	410.0	78.4
5.00	420.0	80.3
6.66	428.0	81.8
10.00	436.0	83.4
20.00	440.0	84.1
40.00	452.0	86.4

Table LXXIII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.10	25.3425	0.5456	24.7969	0.81
0.15	25.5125	0.8184	24.6941	1.22
0.20	25.6900	1.0912	24.5988	1.60
0.30	26.0375	1.6368	24.4007	2.00
0.40	26.3875	2.1824	24.2051	3.18
0.50	26.7300	2.7277	24.0023	3.99
1.00	28.4350	5.4555	22.9795	8.08
1.50	30.0950	8.1833	21.9117	12.35
2.00	31.7625	10.9110	20.8515	16.59
2.50	33.3800	13.6388	19.7412	21.03
3.00	34.9825	16.3665	18.6160	25.54
3.50	36.6100	19.0943	17.5157	29.94
4.00	38.2475	21.8220	16.4255	34.30

Table LXXIV.—Hydrates.

m.	*α.*	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.10	0.834	4.96	5.26	5.22	2.78	27.8
0.15	0.818	4.90	5.16	5.10	2.18	14.5
0.20	0.803	4.85	5.24	5.16	3.33	16.7
0.30	0.784	4.78	5.36	5.25	4.92	16.4
0.40	0.743	4.62	5.54	5.36	7.67	19.2
0.50	0.716	4.52	5.78	5.55	10.31	20.6
1.00	0.597	4.08	6.78	6.23	19.17	19.17
1.50	0.490	3.68	7.64	6.70	25.05	16.7
2.00	0.393	3.32	8.00	6.67	27.90	13.95
2.50	0.300	2.98	9.00	7.11	32.38	12.95
3.00	0.245	2.87	10.40	7.74	34.95	11.65
3.50	0.207	2.63	12.00	8.41	38.18	10.9
4.00	0.134	2.36	14.40	9.46	41.75	10.4

Sodium Hydroxide.

Sodium hydroxide was studied over as wide range of concentration as the solubility would permit. From solutions more concentrated than 6 N the solid separated. The material used was free from carbonate and the solutions were kept in closed vessels during all of the work.

The amount of water combined passes through a minimum (see Fig. V.) at a concentration of about 0.3 N. From this

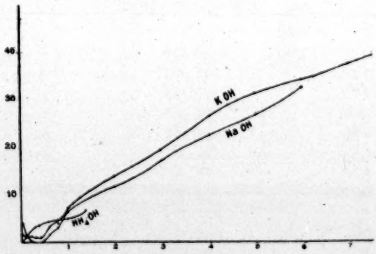


Fig. V.

point it increases with the concentration up to the most concentrated solution. The number of molecules of water in

combination with one of the dissolved substance also passes through a minimum.

Table LXXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.188	3.76
0.1	0°.358	3.58
0.2	0°.693	3.47
0.3	0°.992	3.31
0.4	1°.334	3.34
0.6	2°.030	3.38
0.8	2°.727	3.41
1.0	3°.465	3.465
2.0	7°.40	3.70
3.0	11°.75	3.92
4.0	17°.00	4.25
5.0	23°.00	4.60
6.0	33°.00	5.50

Table LXXVI.—Conductivity Measurements.

$\mu\infty$ 0° = 138.6.

v.	μ_v 0°.	α.
0.125	16.07	11.6
0.143	21.67	15.6
0.166	29.28	21.1
0.200	38.27	27.6
0.250	49.67	35.8
0.333	62.3	44.9
0.500	78.5	57.0
1.00	95.5	63.7
1.25	101.0	71.9
1.66	105.0	75.0
2.50	110.0	79.1
3.33	113.0	81.3
5.00	117.0	83.2
10.00	119.0	85.5
20.00	121.0	87.0

Table LXXVII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Base.}$	W_{H_2O}.	Correction. Per cent.
0.05	25.0550	0.0501	25.0049	—0.02
0.10	25.1000	0.1002	24.9998	0.00
0.20	25.2125	0.2003	25.0122	—0.05
0.30	25.3125	0.3005	25.0120	—0.05
0.40	25.4125	0.4006	25.0119	—0.05
0.60	25.6175	0.6009	25.0166	—0.07
0.80	25.8200	0.8012	25.0188	—0.07
1.00	26.0175	1.0015	25.0160	—0.06
2.00	26.9875	2.0030	24.9845	0.06
3.00	27.8925	3.0045	24.8880	0.45
4.00	28.8300	4.0060	24.8240	0.70
5.00	29.5650	5.0075	24.5575	1.77
6.00	30.3225	6.0090	24.3135	2.35
7.00	31.0900	7.0105	24.0795	3.68
8.00	31.8025	8.0120	23.7905	4.84

Table LXXVIII.—Hydrates.

m.	*a*.	L.	$\frac{\Delta}{m}$.	L′.	*m*′.	H.
0.05	0.870	3.48	3.76	3.76	4.16	83.2
0.10	0.855	3.45	3.58	3.58	2.06	20.6
0.20	0.832	3.42	3.47	3.47	0.87	4.3
0.30	0.813	3.37	3.31	3.31	—	—
0.40	0.791	3.33	3.33	3.33	—	—
0.60	0.750	3.25	3.38	3.38	2.11	3.5
0.80	0.719	3.20	3.41	3.41	3.44	4.3
1.0	0.637	3.04	3.465	3.465	6.83	6.8
2.0	0.570	2.92	3.70	3.70	11.72	5.86
3.0	0.449	2.70	3.92	3.90	17.05	5.68
4.0	0.358	2.53	4.25	4.23	22.33	5.58
5.0	0.276	2.37	4.60	4.52	26.44	5.28
6.0	0.211	2.25	5.50	5.37	32.26	5.37

Potassium Hydroxide.

Potassium hydroxide, free from carbonate, was carefully preserved during the investigation in closed vessels. It could be used up to a concentration that was about 8 N.

The total amount of combined water passes through a minimum at a concentration of about 0.3 N. Similarly, the num-

ber of molecules of water in combination with 1 molecule of the base. In general behavior, respecting its power to combine with water, potassium hydroxide is, then, strictly analogous to sodium hydroxide.

Table LXXIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.183	3.66
0.1	0°.357	3.57
0.2	0°.710	3.55
0.3	1°.050	3.50
0.4	1°.390	3.475
0.6	2°.143	3.571
0.8	2°.885	3.606
1.0	3°.773	3.773
2.0	8°.42	4.21
3.0	14°.0	4.66
4.0	22°.5	5.62
5.0	32°.5	6.50
6.0	43°.5	7.25
7.0	57°.5	8.21
8.0	76°.0	9.50

Table LXXX.—Conductivity Measurements.

$\mu\infty$ 0° = 154.29.

v.	μ_v 0°.	α.
0.111	32.25	20.9
0.125	38.77	25.1
0.143	48.65	31.5
0.166	56.19	36.4
0.200	65.74	42.6
0.250	77.60	50.6
0.333	88.85	58.2
0.500	102.31	66.3
1.000	116.94	75.9
1.250	118.0	76.5
1.660	123.0	79.7
2.500	126.0	82.3
3.333	128.0	83.6
5.000	131.0	85.5
10.00	132.5	86.5
20.00	136.0	89.0

Table LXXXI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Base.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0750	0.0702	25.0048	—0.02
0.10	25.1250	0.1404	24.9846	0.06
0.20	25.2500	0.2808	24.9692	0.12
0.30	25.3750	0.4212	24.9538	0.18
0.40	25.4925	0.5616	24.9309	0.28
0.60	25.7373	0.8424	24.8949	0.42
0.80	25.9700	1.1232	24.8458	0.62
1.0	26.2050	1.4040	24.8010	0.80
2.0	27.3150	2.8080	24.5070	1.97
3.0	28.3500	4.2120	24.1380	3.45
4.0	29.4025	5.6160	23.7865	4.85
5.0	30.3600	7.0200	23.3400	6.64
6.0	31.2675	8.4240	22.8435	8.63
7.0	32.1825	9.8280	22.3545	10.58
8.0	33.3075	11.2320	22.0755	11.71

Table LXXXII.—Hydrates.

m.	*α.*	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.05	0.890	3.52	3.66	3.66	2.11	42.2
0.10	0.865	3.47	3.57	3.57	1.56	15.6
0.20	0.855	3.45	3.55	3.55	1.56	7.8
0.30	0.836	3.41	3.50	3.49	1.28	4.3
0.40	0.823	3.39	3.475	3.47	1.28	3.2
0.60	0.797	3.34	3.57	3.56	3.42	5.7
0.80	0.765	3.28	3.61	3.58	4.67	5.8
1.0	0.759	3.27	3.77	3.74	6.94	6.9
2.0	0.663	3.09	4.21	4.13	14.05	7.0
3.0	0.582	2.94	4.66	4.50	19.28	6.4
4.0	0.506	2.80	5.63	5.36	26.55	6.6
5.0	0.426	2.65	6.50	6.07	31.15	6.2
6.0	0.364	2.54	7.25	6.63	34.30	5.7
7.0	0.315	2.45	8.21	7.34	37.00	5.3
8.0	0.251	2.33	9.50	8.39	40.10	5.0

Ammonium Hydroxide.

Ammonium hydroxide was studied in a manner similar to the other bases. The freezing-point lowerings were small but, since the dissociation is so very slight, it, nevertheless, demon-

strates the possession, by this compound, of some power to combine with water.

The amount of combined water increases from the most dilute to the most concentrated solutions (see Fig. V.). The amounts of water combined with 1 molecule of the base, while somewhat irregular, in general, increases with the dilution.

Table LXXXIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.0961	1.92
0.10	0.192	1.92
0.20	0.384	1.92
0.30	0.591	1.97
0.40	0.791	1.98
0.60	1.191	1.98
0.80	1.585	1.98
1.00	1.995	1.995
1.4036	2.865	2.04

Table LXXXIV.—Conductivity Measurements.

$\mu\infty$ 0° = 154.69.

v.	μ_v 0°.	α.
1.0	0.41	0.26
1.25	0.59	0.38
1.66	0.76	0.49
2.50	0.93	0.60
3.33	1.08	0.70
5.00	1.34	0.86
10.00	1.84	1.19
20.00	2.56	1.66

Table LXXXV.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Base.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	24.9775	0.0426	24.9349	—0.26
0.10	24.9625	0.0852	24.8773	—0.49
0.20	24.9425	0.1704	24.7721	—0.91
0.30	24.9250	0.2556	24.6694	—1.32
0.40	24.9050	0.3408	24.5642	—1.74
0.60	24.8625	0.5112	24.3513	—2.59
0.80	24.8250	0.6816	24.1434	—3.43
1.00	24.7925	0.8520	23.9405	—4.21
1.4036	24.7150	1.1928	23.5222	—5.91

Table LXXXVI.—Hydrates.

m.	α.	I..	$\frac{\Delta}{m}$.	I.′.	m'.	H.
0.05	0.0166	1.89	1.92	1.92	0.87	17.4
0.10	0.0119	1.88	1.92	1.93	1.73	17.3
0.20	0.0086	1.88	1.92	1.94	1.72	8.6
0.30	0.0070	1.87	1.97	2.00	3.61	12.0
0.40	0.0060	1.87	1.98	2.01	3.82	9.5
0.60	0.0049	1.87	1.98	2.03	4.38	7.3
0.80	0.0038	1.87	1.98	2.05	4.88	6.1
1.00	0.0026	1.86	1.995	2.08	5.88	5.9
1.4036	—	1.86	2.04	2.16	7.72	5.5

General Discussion of Results.

The amount of work that has now been done in this field, *involving between 90 and 100 compounds and between 1,200 and 1,500 solutions*, seems to make it desirable, if not absolutely necessary, to take a general survey of the subject at the present stage of the investigation. This is all the more needful, in that the various papers have been published in different scientific journals.

The whole work was the outcome of observations made in this laboratory, about 6 years ago, by Jones and Ota[1] and Jones and Knight ;[2] that certain salts, in concentrated solution, give abnormally great lowering of the freezing-point of water. The problem was taken up by Jones and Chambers[3] and studied for a number of chlorides and bromides. As the result of this work Jones[4] concluded that "In concentrated solutions these chlorides and bromides must take up a part of the water forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit or as one molecule in lowering the freezing-point of the remaining water. The total amount of water present, which is now acting as solvent,

[1] THIS JOURNAL, **22**, 5 (1899).
[2] *Ibid.*, **22**, 110 (1899).
[3] *Ibid.*, **23**, 89 (1900).
[4] *Ibid.*, **23**, 103 (1900).

is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules. By assuming that a molecule of the halide is in combination with a large number of molecules of water, it is possible to explain all the freezing-point results obtained." At the suggestion of Jones, this work was continued by Chambers and Frazer,[1] and results of the same general character were obtained.

The investigation was then taken up in a more systematic manner by Jones and Getman.[2] They studied a variety of acids, bases and salts and found that the phenomenon previously observed was general—most substances giving, in concentrated solutions, freezing-point lowerings that were greater than the theoretical value.

In the following year, Jones and Getman, aided by a grant from the Carnegie Institution, continued their former work and calculated the approximate composition of the hydrates formed by a number of substances.[3]

Through another grant from the Carnegie Institution, Jones and Bassett have still further continued the work. They have had to do especially with the determination, as closely as possible, of the composition of the hydrates formed. The first part of this investigation has already been recorded;[4] the results of the second part are contained in this paper.

Evidence for the Existence of Hydrates in Solution.

Four distinct lines of evidence bearing upon the hydrate theory have been pointed out. In the first place, the ***minima in the boiling-point curves manifest themselves at greater concentrations than in the freezing-point curves.*** This is just what would be expected in terms of our hydrate theory, since, at the higher temperatures, the hydrates would be less stable and a greater concentration would have to be reached before there

[1] THIS JOURNAL, **23**, 512 (1900).
[2] Z. physik. Chem., **46**, 244 (1903). THIS JOURNAL, **27**, 433 (1902).
[3] THIS JOURNAL, **31**, 303 (1904); **32**, 308 (1904). Z. physik. Chem., **49**, 385 (1904).
[4] THIS JOURNAL, **33**, 534 (1905).

was sufficient hydration to change the direction of the curve and produce a minimum.

The second line of evidence, which is more direct, has to do with the *relation between water of crystallization and lowering of the freezing-point.* This has already been pointed out.[1] Curve plates have been drawn, which show this relation very clearly. The chlorides stand in the same order with respect to their power to lower the freezing-point of water and with respect to their power to combine with water, as water of crystallization. The same relation holds for the various bromides and iodides that have been investigated.

Turning to the nitrates, the relations are just as satisfactory. When all of the nitrates with which we have worked are plotted on the same curve sheet, the ordinates being molecular lowerings of the freezing-point and the abscissas concentrations, we find a most satisfactory relation between water of crystallization and molecular lowering of the freezing-point.

In the above comparisons the acid is kept constant in every case and the salts of it with the different metals are compared with one another. It has also been shown[2] that similar relations exist between the salts of any given metal with different acids. If we compare the chlorides, bromides, iodides and nitrates of any given metal, having the same number of molecules of water of crystallization, they give just about the same molecular lowering of the freezing-point of water. As such comparisons have so recently been discussed,[3] reference only will be made to them.

The relation just referred to is exactly what would be expected if our hydrate theory is true. Indeed, it is difficult to see in what other way it can be interpreted. The relation is closer and much more comprehensive than we could ever have anticipated. In the building up of crystals, the exact geometrical shape of the molecules is undoubtedly a fundamental matter and this would condition, to some extent, the number of molecules of water with which any given salt would crystal-

[1] This JOURNAL, **31**, 344 (1904). Z. physik. Chem., **49**, 385 (1904). THIS JOURNAL, **32**, 308 (1904); **33**, 534 (1905). J. Chim. Phys., **3**, 455 (1905).

[2] THIS JOURNAL, **33**, 540 (1905).

[3] *Ibid.*, **33**, 541 (1905).

lize. Notwithstanding this and other influences which affect the molecules as they build up crystals, relations, such as those already pointed out, manifest themselves very clearly.

Again, we have searched for a salt with a larger number of molecules of water of crystallization than that possessed by the nitrates of chromium and iron, which is 9, and which would be adapted to our work. The salts of chromic and dichromic acids would not help us, since these, like the sulphates, probably undergo polymerization in solution and would give abnormal results. The best example that we could find was disodium phosphate, with 12 molecules of water of crystallization. The unfortunate feature in connection with this salt is its slight solubility in water, especially at the freezing temperature. We were able to work at two concentrations, 0.05 and 0.1 N and, although the experimental error at these high dilutions is relatively large, we feel justified in drawing the conclusion that this salt has greater power to combine with water than any other compound which we have studied.

Two other lines of evidence bearing upon our hydrate theory, the one having to do with the effect of temperature upon water of crystallization and the other with certain changes in color produced in solution, have already been discussed in the earlier part of this paper and will, therefore, be only referred to here. The reaction between crystallized calcium chloride and an aqueous solution of cobalt chloride shows, conclusively, that a salt can combine with more water in solution than it can bring with it out of solution, as water of crystallization.

Composition of the Hydrates.

The work of the present year has had to do with the determination of the composition of the hydrates formed by the various substances at the different dilutions. While certain assumptions are necessary in making these calculations, yet, taking all things into account, it seems to us probable that we can calculate the approximate composition of the hydrates that exist in the aqueous solutions. The method of calculation has already been discussed. It, therefore, remains only to con-

sider the results, the most reliable of which are contained in the paper recently published[1] and in the present communication.

If we examine these results, we shall see that the total amount of water held in combination by the dissolved substance increases with the concentration of the solution. This is, of course, what would be expected from the law of mass action. If we examine column "*m*" in the "Hydrate" tables we shall see how general this relation is. There are comparatively few deviations from this relation, with the exception of some dilute solutions where the experimental errors are necessarily large.

If we turn to column "H" in the "Hydrate" tables, we have the number of molecules of water combined with 1 molecule of the dissolved substance. The general relation here is, that the number of molecules of water combined with 1 molecule of the dissolved substance, increases with the dilution, from the most concentrated to the most dilute solution investigated. This is shown by such substances as magnesium chloride, magnesium bromide, manganese chloride, nickel chloride, nickel nitrate, copper chloride, strontium nitrate, chromium chloride, sodium ammonium acid phosphate and others. In some cases irregularities manifest themselves, but these are, doubtless, often due to a summation of experimental errors.

If we turn to the acids a different relation appears. Take hydrochloric, hydrobromic, nitric and sulphuric acid.[2] Starting with the more concentrated and passing to the more dilute solutions, we find that the number of molecules of water in combination with 1 molecule of the acid, passes through a maximum. In the case of the four acids already mentioned, this maximum is reached at about 2 N solution.

A possible explanation of this phenomenon, which is in keeping with the law of mass action, is the following: If the attraction of the dissolved molecule for water is slight then, when a certain dilution is reached, the effect of the presence of

[1] THIS JOURNAL, 33, 534 (1905).
[2] *Ibid.*, 33, 581 (1905).

more water might actually diminish the amount of water combined with a molecule of the dissolved substance. When the number of molecules of water had become sufficiently great, their attractions for one another would summate, and might overcome, in part, the attraction of the dissolved substance for the water. In this case the *complexity of the hydrate would pass through a maximum and then decrease with further dilution.*

Most of the organic compounds studied by Jones and Getman[1] show little or no power to combine with water. Glycerol, however, is a marked exception and cane-sugar also has considerable hydrating power. The total amount of water combined with the dissolved substance, in both cases, increases with the concentration, as we should expect. The number of molecules of water combined with 1 molecule of the dissolved substance, in the case of glycerol, increases, with a fair degree of regularity, with the dilution of the solution.

A number of organic acids were studied and shown to have little or no power to combine with water.

Both molecules and ions combine with water. Our opinion on this point has changed from time to time as the work has developed. Since such non-electrolytes as glycerol and cane-sugar can form hydrates, it is obvious that molecules can combine with water, because there are no ions present in such solutions. In the case of electrolytes, on the other hand, we frequently have the greatest hydration in the most dilute solutions. In such solutions there are very few molecules present, nearly all of them being broken down into ions. It is evident that the ions can combine with water. Our final conclusion is that both molecules and ions can combine with water and form hydrates.

The present theory of hydrates differs fundamentally from the older theory. It may not be obvious, at first sight, how the hydrate theory proposed by Jones differs from the older hydrate theory of Mendeléeff. A moment's thought, however, will show that the two are fundamentally different. According to the view of Mendeléeff, a compound such as calcium chloride or sulphuric acid, with water, forms three or four hy-

[1] THIS JOURNAL, 32, 308 (1904).

drates, having perfectly definite compositions and containing very different amounts of water; *e. g.*, $H_2SO_4.H_2O$; $H_2SO_4.2H_2O$; $H_2SO_4.6H_2O$; $H_2SO_4.150H_2O$. These hydrates and no intermediate ones, exist.

According to the present theory, a compound such as calcium chloride *can form all the possible hydrates with water, from one or a few molecules of water up to at least 30 molecules.* The composition of the hydrate is conditioned by the concentration of the solution, temperature being constant.

It is possible, indeed, quite probable, that several hydrates, having different compositions, exist simultaneously in every solution. We cannot, of course, distinguish between this possibility and the simpler one—that at any given concentration only one hydrate, with a perfectly definite composition, exists.

Work by the boiling-point method has shown that dissolved substances can combine with solvents other than water. This has been demonstrated by Jones and Getman[1] to be the case with at least methyl and ethyl alcohols.

Summary of the Conclusions Thus Far Reached.

1. This investigation has already been extended to between 90 and 100 compounds, including salts, acids and bases, and between 1,200 and 1,500 solutions have been studied.

2. The freezing-point, the conductivities at 0° and the specific gravities of all the solutions have been measured, and the refractivity of a large number of them.

3. Four lines of evidence bearing upon the hydrate theory have been deduced and all of these point to its general correctness. These are, the relative positions of the minima in the freezing-point and in the boiling-point curves; the relation between water of crystallization and lowering of the freezing-point; the effect of temperature of crystallization on the amount of water of crystallization, and the power of substances to combine with more water in solution than they can bring with them out of solution, as shown by the change in color of

[1] THIS JOURNAL, **31**, 339 (1904); **32**, 338 (1904).

a solution of cobalt chloride when shaken with crystallized calcium chloride.

4. The approximate composition of the hydrates formed by a fairly large number of electrolytes and some non-electrolytes have been calculated. Those substances that crystallize without water have little or no hydrating power. In general, the larger the number of molecules of water of crystallization the greater the hydrating power of the salt.

5. The total amount of water in combination with the dissolved substance increases with the concentration of the solution. The number of molecules of water in combination with 1 molecule of the dissolved substance usually increases with the dilution of the solution.

6. In some cases, as with the more common acids, the amount of water in combination with 1 molecule of the dissolved substances passes through a maximum as the dilution is increased. A possible explanation of this fact has been suggested.

7. A number of organic compounds have been studied, but only a few of these have been found to have any marked hydrating power.

8. Certain substances have been shown to have the power to combine with solvents other than water. Work, thus far, has been limited to methyl and ethyl alcohols.

9. It has been pointed out that the hydrates formed in aqueous solutions are unstable, especially at higher temperatures. They are, in general, broken down at the boiling-points of the solutions, all of the water escaping except what is held in combination by the salt, as water of crystallization.

10. As the result of our work as a whole, we must conclude that both molecules and ions have the power to combine with water in aqueous solutions and form hydrates.

11. The new hydrate theory differs fundamentally from the old, in that, according to the former, we have a series of hydrates formed by the dissolved substance having all possible compositions up to a given maximum—the composition depending on the concentration, as we should expect from the law of mass action.

12. The bearing of this work on the general theory of solutions is obvious. The fact that a part of the water is combined with the dissolved substance and is not acting as solvent water, must be taken into account in dealing with all solutions and especially with concentrated ones. This accounts, in large part, for the abnormal behavior of concentrated solutions and is, doubtless, an important factor in the apparent failure of the gas laws to apply to such solutions. When this is taken into account, together with such other factors as appear in Van der Waals' equation for gases, it will probably be shown that the gas laws apply to the osmotic pressures of concentrated solutions measured under comparable conditions with gases, as well as to concentrated gases.

This line of work is still in progress in this laboratory and will be continued for some time to come.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1905.

OBITUARY.

PER THEODOR CLEVE.

Professor Cleve was born at Stockholm, February 10, 1840, and died at Upsala, June 18, 1905. He graduated from the University of Upsala in 1863 and has held the chair of chemistry there since 1874. After graduation he studied under Wurtz and, before returning to Upsala, taught for 4 years in the Stockholm Polytechnic. Cleve's chemical activities covered a wide range, although he is best known for his work on the rare earth metals. We owe the discovery of thulium to him (1880), of scandium (1890) independently of Nilson and of helium (1895) independently of Ramsay. He was the first to observe the isomerism of the platinumamine derivatives. Cleve's scientific efforts were not confined to chemistry but included geology, botany and hydrography; his contributions to general literature were also noteworthy. He received the Davy medal from the Royal Society in 1904, and was president of the committee for chemistry of the Nobel Trust.

REVIEWS.

ELEMENTS OF APPLIED MICROSCOPY. By CHARLES EDWARD AMORY WINSLOW, Instructor in Industrial Microscopy and Sanitary Biology in the Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1905. pp. xii + 183. Price, $1.50.

This little work is intended especially for the use of beginners in microscopical examinations, but it will be also valuable to many experts. The first section describes the various parts of microscopic apparatus, care of eyes, etc., and will be especially useful for beginners, but Chapter III. and the following ones contain much that is helpful to workers in general. There is a large part of the book which is especially useful to those engaged in the examination of foods and fibers and, therefore, it is particularly valuable to workers in agricultural research. There are interesting chapters also on the microscope as applied to medicine, sanitation and to cases in courts, while the chapter on microchemistry will be of service to chemists in general. The chapter on petrography will be especially useful to those who are working with minerals and the chemistry or physics of materials used in road-making. The book contains 60 illustrations, which are of distinct advantage in the elucidation of the text. As is necessarily the case in a volume of this kind, the material is more for the purpose of illustration and suggestion than for detailed description or discussion.

The bibliography at the end of each chapter will refer the inquiring student to more exhaustive works and this feature of the book might have been made more extensive without adding materially to its size, while increasing its usefulness for advanced students. The character of those who are beginning the study of the microscope is so varied, representing as it does all stages from childhood to old age, that the preparation of a book of this character is an exceedingly difficult matter. The volume shows, however, that the author has covered this point and rendered his work helpful to students of almost every class.

H. W. W.

THE PRINCIPLES OF CHEMISTRY. By D. MENDELÉEFF. Third English Edition translated from the Russian Seventh Edition by GEORGE KAMENSKY, A.R.S.M., of the Imperial Mint, St. Petersburg, and edited by THOMAS H. POPE, B.Sc., F.I.C., in two volumes. London and New York: Longmans, Green & Co. 1905. Price, $10.00 net.

The first edition of this work was reviewed 13 years ago by President Remsen.[1] While one finds new and interesting mat-

[1] THIS JOURNAL, 14, 251.

ter in this last edition, the character of the work remains unchanged. The foot-notes still form nearly half of the contents and are full of philosophical thought, of originality and suggestions.

A quotation from the preface to this edition will show Mendeléeff's attitude:

"After having been an insignificant but zealous worker in chemistry for almost half a century, I wished that my book should retain some traces of how a confirmed disciple of Gerhardt regards the fundamental problems of the theory of the chemical elements at the beginning of the twentieth century. As an example, I may mention that the more I have thought on the nature of the chemical elements, the more decidedly have I turned away from the classical notion of a primary matter and from the hope of attaining the desired end by a study of electrical and optical phenomena and the more clearly have I recognized that first and foremost are needed truer conceptions of 'mass' and 'ether' than those in vogue at the present time. The return to electro-chemism, which is so evident in the supporters of the hypothesis of 'electrolytic dissociation,' and the notion of the splitting up of atoms into 'electrons,' in my opinion only complicate and in no way explain so real a matter as the chemical changes of substances, which led to the recognition of the invariable and ponderable atoms of simple bodies."

As Mendeléeff does not consider the hypothesis of electrolytic dissociation and the hypotheses deduced from it to be "in accordance with fact," and as he devotes much space in text and notes to osmotic pressure, nature of solutions, relation of gas and solution laws, it is very interesting to read his interpretation of facts from a point of view differing radically from that of Arrhenius and Ostwald.

One looks for his views on the subject of radioactive substances. In discussing them in a note under "Uranium" he says: "The greatest known concentration of mass of ponderable matter in the indivisible mass of the atom of uranium should already—*a priori*—produce peculiar qualities, although I am not in any way inclined (owing to the stern but fruitful discipline of inductive knowledge) to admit even the hypothetical transmutation of the elements into each other and see no possibility of argon or radio-active substances having originated from uranium, or conversely." It must be noted that this was published in Russia in 1902, prior to Ramsay's work on radium emanation and helium.

Enough has been said to point out the independent position

which Mendeléeff holds, and it is this which makes his book so valuable and so fascinating to those who turn with weariness from the last repetition of what we all knew before of the average text-book. It is fair to say that most of these choice morsels are in the notes and Mendeléeff warns students against reading the notes, evidently thinking them too strong meat for chemical babes.

Appended to the translation are his Royal Institution lecture of 1889, his Faraday lecture of the same year on the periodic law and his recent essay on "An Attempt toward a Chemical Conception of the Ether." This last was quite recently reviewed by President Remsen.[1]

A few words may be given to the first of these lectures. Its object was to show that—"starting with Newton's third law of motion, it is possible to preserve to chemistry all the advantages arising from structural teaching without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities." He says, further on, "It will be seen that by the principle of substitution, that is, by the third law of Newton, we are able to deduce in the simplest manner not only the individual composition, the isomerism and relation of substances, but also the general laws which govern their most complex combinations without having recourse either to statical constructions, to the definition of atomicities, to the exclusion of free affinities, or to the recognition of those single, double, or treble bonds which are so indispensable to structuralists in the explanation of the composition and construction of hydrocarbon compounds."

This, too, is very interesting coming from a pupil of Gerhardt, who never accepted the structural theories of Kekulé.

E. R.

MARCELI NENCKI OPERA OMNIA. Gesammelte Arbeiten von PROF. M. NENCKI. Braunschweig: Friedrich Vieweg und Sohn. 1905. Volume I., pp. 840; Volume II., pp. 893. Price, M. 45.

It is certainly a well-deserved honor to the memory of Nencki that this posthumous publication of his collected reprints should have appeared. The fact that it is edited by his ardent admirers and associates, Sieber and Zaleski, gives sufficient assurance of its accuracy and completeness. They have brought together the 346 widely scattered articles from Nencki's laboratory which appeared in German, French, Russian and Polish journals from 1869 to 1901. Of these articles Nencki's name is attached to somewhat less than half the number. The re-

[1] THIS JOURNAL, 33, 517.

mainder appeared under the names of the many brilliant pupils attracted to the laboratory of this indefatigable worker, who prided himself on the fact that he was too busy to attend scientific meetings. As the subjects of the papers, however, were always suggested by Nencki and were executed under his supervision, it is only proper that they should appear in his "Opera Omnia." Although Nencki concerned himself with many different branches of science, organic chemistry, physiological chemistry, pharmacology, bacteriology and hygiene, his fame rests principally on his brilliant contributions to physiological chemistry. It is, indeed, difficult to give a just idea of Nencki's work within the limits of a review. His principal contributions to organic chemistry consisted in the synthesis of many compounds which he believed might throw light on physiological processes. Thus he synthesized many urea and guanidine derivatives, in connection with his work on the precursors of urea and its mode of formation in the body. The work of Nencki and his pupils on the decomposition-products of haemoglobin is classic. They showed haematoporphyrin to be isomeric with bilirubin, thus establishing, clearly, the derivation of the bile pigments from haemoglobin. They proved, further, that haemoglobin is closely related to chlorophyll and determined the structure of haomatoporphyrin and phylloporphyrin, from both of which they obtained haemopyrrol. This genetic and chemical relation so firmly established is, to be sure, of broad biological interest. Nencki's work on the chemical transformations of numerous aromatic substances in passing through the body, his work on the enzymes, putrefaction and immunity can only be mentioned here to give an idea of the scope of his work. While not a genius, Nencki represents the type of the brilliant investigator. The real advance in a science depends on the steady stream of such laborious researches as those executed in his aboratory.

An excellent photogravure of Nencki and a specimen page of his manuscript make the memorial a most complete, pleasing and impressive one. The work would be a valuable addition to any chemical or medical library. A. S. L.

AVOGADRO AND DALTON. THE STANDING IN CHEMISTRY OF THEIR HYPOTHESES. By ANDREW M. MELDRUM, D.Sc. With a preface by FRANCIS R. JAPP, M.A., LL.D., F.R.S., Professor of Chemistry in the University of Aberdeen. Edinburgh: William F. Clay, 18 Teviot Place. 1904. Price, 3 Shillings, net.

In the preface Professor Japp says: "The important question whether, in discussing the constitution of matter, the

atom or the molecule should be first considered is one regarding which there has been considerable difference of opinion among chemists." . . . . "In the study of the constitution of matter . . . . . we are compelled by the very nature of the particular problems of scientific measurement and calculation involved, to reverse what is, apparently, the natural order of things and to proceed from the more complex to the simpler—from highly complex objects of sense to successively simpler and simpler conceptual structures underlying these. Thus the order of quantitative determinations is: (1) Relative weights of comparable amounts of *matter in bulk* (gaseous or dissolved); (2) relative weights of *molecules*; (3) relative weights of *atoms*; and (4) if subsequent experiments should justify the most recent speculations, mass of *electrons*."

"The view here stated as to the true ratiocinative order of precedence of the molecular and atomic hypotheses has been held by various chemists; I have nowhere else seen it expounded with such wealth of illustration and with so extensive a knowledge of the fundamental literature of the subject as in the present monograph by Dr. Meldrum."

The pamphlet of 113 pages is divided into two parts. Part I. treats of the standing in chemistry of Avogadro's hypothesis, and Part II. of the standing in chemistry of Dalton's Atomic Theory.

The author is of the opinion that the services of Dalton have been overestimated. In one place he says: "In the composite man of science, to whom Roscoe gives the name of Dalton, it is easy to discern the features of Charles, Gay-Lussac and Lavoisier. Plainly, the effect of all this is to obscure the individuality of Dalton and in his interests, therefore, to justify and make indispensable an impartial inquiry into his merits."

A careful study of this book would help chemists, whether young or old, to see some of the fundamental problems of their science in a clearer light than usual. It is cordially recommended. I. R.

LABORATORY STUDIES FOR BREWING STUDENTS. By ADRIAN J. BROWN. London and New York: Longmans, Green & Co. 1905. Price, $2.50.

The title of this volume suggests its purpose. It is designed for students of brewing who are under the guidance of an instructor. The laboratory directions, as a whole, are very helpful and those relating to chemical work represent the methods in vogue in England. Although this book should be of considerable value to a beginner in brewing studies, the methods advocated for the analyses of raw materials do not

harmonize with American practice. The author is evidently unacquainted with several publications[1] dealing with acid starch conversions and the analyses of the resulting products. The reviewer, therefore, cannot endorse the processes given for such work. The presence of dextrins in glucose (syrup) is certainly of sufficient importance to brewing students to warrant inserting methods for its estimation, which, unfortunately, are omitted in this volume.

In addition to the chemical side of brewing materials, sufficient directions in elementary bacteriology and yeast culture are given, supplemented by convenient references to more elaborate works, for those who desire extended investigation in the lines indicated. GEORGE DEFREN.

THE NEW KNOWLEDGE. A Popular Account of the New Physics and the New Chemistry in Their Relation to the New Theory of Matter. By ROBERT KENNEDY DUNCAN, Professor of Chemistry in Washington and Jefferson College. Illustrated. New York: A. S. Barnes & Company. 1905. pp. 263. Price, $2.00 net.

The author has made a good selection of material for this book. It is written with enthusiasm. Indeed, this not infrequently is present in such excess as to lead dangerously near to the sensational. There is a lack of perspective in the work, due, in part, to the author's attitude toward the historical method, which he characterizes, in his preface, as "the death of clear exposition."

Any discussion of modern discoveries, which ignores what has been done in the past, is liable to value unduly the newest developments, and this is a serious defect in the present book. From this work, alone, one would conclude that most of the science of the last century was now obsolete. Indeed, it is stated in the preface that "where before there was solid walking ground to the older science now there is nothing but shifting sand." This is liable to leave an entirely erroneous impression, especially upon the popular mind.

Again, inaccuracy of statement is not infrequent. A few examples will make the above points clear.

That "the properties of ether are for the most part negative" (p. 3) or that "the doctrine of the conservation of energy is receiving some hard knocks nowadays" (p. 7) will scarcely receive the sanction of the leading physicists.

Similarly, the physical chemist will not be convinced, in speaking of positive ions, that "their electrical charge is of the same order as that of an ordinary atom" (p. 76), since

[1] J. Am. Chem. Soc., **18**, 748, 869. [Revised in Technology Quarterly, **10**, 133]; *Ibid.*, **19**, 261; **25**, 1003.

atoms are uncharged. Further, the term "order," as here used, is ambiguous.

The paragraph on valency (pp. 166–167) is without the proper perspective. We knew that "it was electrical in its origin" before the discovery of the "electron." That Faraday's Law is the basis of valency has been pointed out frequently by the reviewer and has been made the basis of the discussion of this subject in both his Physical and Inorganic Chemistries.

On p. 167 it is stated that "a univalent positive atom is one which, under the circumstances of chemical action, attains stability by losing one, and only one, corpuscle." This sentence contains an unusual number of errors. In the first place, an atom is always uncharged and is, therefore, neither positive nor negative. Evidently an ion is meant. Secondly, in terms of this statement, we should have valency only "under the circumstances of chemical action," which is meaningless. Thirdly, what is lost is not a "corpuscle" but an electron. The author fails, repeatedly, to distinguish between the two.

The statements about the formation of helium from the radium emanation and concerning the relations of alchemy to modern chemistry, could be advantageously revised.

It should have been pointed out that the positive particles, corresponding to the negative electrons, probably exist in the "canal or anode rays" discovered by Goldstein.

It appears, to the reviewer, that the style of the book would have been more dignified and more conclusive to cool, scientific thought, had such headings as the following been omitted, or at least revised: "*A New Use for Clouds*," "*Discovery of the One Thing*," "*Celestial Dissociation*," "*The Reconstruction of a Universe*," etc.

The author of this book has undoubtedly followed closely the recent developments in the physical sciences and his work is, for the most part, clear and interesting. It is unfortunate that it should contain such serious defects. H. C. J.